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THE ADSORPTION OF THORIUM B AND THORIUM C FROM SOLUTION

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INTRODUCTION

Paneth (1) in his Baker Lectures has shown how, with the development of the knowledge of the chemistry of the socalled radioelements, there has come about an increasing use of these elements in studying some of the well-known chemical problems. Fajans (2), Paneth (3), and Hahn (4)[1] have made use of these radioelements in studies of the causes and mechanism of adsorption from solution. The phenomenon of adsorption is one of the most studied of chemical problems and the chemical literature is full of observations of the adsorption of many adsorbed substances by numerous adsorbents. A great deal of this work on adsorption has been carried out with difficultly defined adsorbents and with more or less complex adsorbed substances. Although these studies give valuable data because they record observations of common chemical systems as they actually exist, yet the number of variables involved makes the interpretation of the data in simple terms very difficult. The work of Fajans and others has reduced the study of adsorption to a simple system, that of a salt-like crystal as adsorbent and a single simple ion as the adsorbed substance. Because methods of analysis limit the accuracy of a quantitative study of the amount of ions removed by an adsorbent, these workers have made use of the electroscope for measuring quantitatively the number of radioactive ions which have been removed from solution. By use of this method it has been possible to measure on a rather small surface of a crystal adsorbent not only the amount of radioactive ions which have been removed from solution but also indirectly (using the radioactive ions as indicators) the amount of the ions of some of the common elements and of radicals which could not be detected in micro quantities by the ordinary methods of analysis.

From the results of the experiments just referred to, Fajans, Paneth, and Hahn have formulated rules for adsorption from solution. (For a state-

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[1] In references 1 to 4 are to be found most of the references to work which has been done in the field of the articles to be presented.

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ment and discussion of these rules see reference 2.) In these rules there is shown a relation between adsorption and mixed crystal formation, adsorption and solubility (see also Taylor and Beekley (5)) and more recently (by Fajans in his expanded rule) adsorption and weakness of dissociation of the compound formed by the adsorbed ion and the oppositely charged ion of the adsorbent.

It is the purpose of this series of three papers to report work which was started under the direction of Professor Fajans[2] in his laboratory in Munich and continued here in this laboratory, giving results which add additional information to the subject of the cause and mechanism of the adsorption of ions from solution. This first paper is to deal in general with the special technique used in all the work and to take up some of the sources of error in measurements in which the thorium B and thorium C equilibrium is concerned. The second paper will report results of the adsorption of thorium B ions on thallium bromide and iodide and the influence of different ions in the solution on this adsorption. The third paper will be concerned with the adsorption of thorium B ions on silver bromide from solutions of varying concentrations of different bromides.

Thorium B, an isotope of lead, is a desirable ion for use in a study of the adsorption of ions on insoluble halide crystals because:—

1. Its half-life of 10.6 hours permits it to be used in an adsorption experiment and then easily determined by the electroscopic method.
2. It can be very easily obtained from the emanation from a sample of radiothorium.
3. Its halides are insoluble.

For this work a β-ray electroscope was used.[3] Since the beta particles emitted from thorium B are so slow that 99 per cent of them can be absorbed by 0.4 mm. of aluminum (6), they cannot conveniently be used for determining the amount of thorium B present. From the disintegration table (7) it can be seen that from the successive disintegration products of thorium B, there are two, thorium C and thorium C_1, which emit alpha particles and two, thorium C and thorium C_2, which emit beta particles. When radioactive equilibrium has been established, the activity due to thorium C_2 is about 5 per cent of the total activity and its half-life is short enough to bring it to equilibrium quickly. The thorium C_1 comes into equilib-

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[2] The senior author of this article (and of two to follow) takes this opportunity to express his gratitude to Professor Dr. K. Fajans, Director of the Institute for Physical Chemistry of the University of Munich, for his suggestions and his kind help and consideration in preparing the material for these papers, not only in his own private laboratory in Munich in 1928, but also while he was Baker Professor of Chemistry in Cornell University in 1930 and twice visited this laboratory.

[3] This electroscope was of design similar to that described in Ostwald-Luther's Physiko-Chemische Messungen, 4th ed., chap. 21.

rium instantaneously with thorium C and need not be considered as separate from it. By either alpha or beta particle measurements, then, the whole activity may be considered to be that of thorium C.

From the relations given by Rutherford can be constructed (1) the activity curve for thorium B alone; (2) the activity curve for thorium B if thorium B and thorium C were in equilibrium with a constant source of thorium B and that source were removed; (3) the activity curve of thorium B if thorium B were pure at zero time and the equilibrium between thorium B and thorium C were then reached.

It can be calculated, or roughly seen from the curves, that after eight hours the course of the three curves is the same to better than 1 per cent and that after ten hours to better than 0.2 per cent. Any measurement, whether of alpha or beta particle activity after these periods of time, will indicate the amount of thorium B present to the accuracy mentioned. The measurements in the present work were made on an equilibrium mixture of thorium B and thorium C. Since with thorium B we are dealing with a lead isotope and with thorium C with a bismuth isotope, consideration will have to be given to the chemistry of these common elements. The adsorption experiments were conducted on thorium B ions, but the disintegration product, thorium C, was used to determine the amount of thorium B present. In handling the radioactive solutions, therefore, attention had to be given to all conditions which disturbed an equilibrium mixture of thorium B and thorium C ions. This first paper is to consider factors involved in the preparation and handling of the radioactive solutions for the subsequent adsorption measurements.

I. THE COLLECTION OF THORIUM B

The source of active material for the measurements, which extended over a period of three years, was a sample of radiothorium of about 3 milligram equivalence, kindly furnished us by the Welsbach Company; later to this was added another sample of 1.5 milligram equivalence procured from the University of Missouri. The emanation from this radiothorium was collected on platinum loops in the collector shown in figure 1. The scale gives the sizes of the different parts.

This collector was connected through a water resistance to a 125- or a 300-volt battery. Assuming the radiothorium is in equilibrium with thorium X and assuming that all the thorium A from the decomposition of the thorium emanation is deposited on the loops, the time for thorium B on the loops to reach equilibrium can be calculated from the decay constants. Sixty-four hours is the time required to deposit 98.4 per cent of the equilibrium amount.

II. THE PREPARATION OF RADIOACTIVE SOLUTIONS

The active deposit was dissolved off the platinum loops with nitric acid. A study was made of the rate of solution of this active deposit in 1 *N*, 0.2 *N* and 0.1 *N* nitric acid. From this study it was found that standing in 0.2 *N* nitric acid at room temperature for from five to ten minutes was sufficient to dissolve off most of the active deposit. Since the acidity of the radioactive solution had to be controlled, the amount of 0.2 *N* nitric acid used depended on the subsequent use which was made of the solution; this will be described later. This nitric acid solution was then transferred to a 100-cc. volumetric flask and made up to volume with distilled water. In order to be sure that the solution as prepared had the desired amount of activity, a 1-cc. sample was pipetted (after rinsing the pipette several times with the solution) on a watch glass and evaporated to dryness. The activity of this sample was measured by use of the beta ray electroscope and the remaining solution was then diluted with nitric acid of the same concentration to give the desired activity.

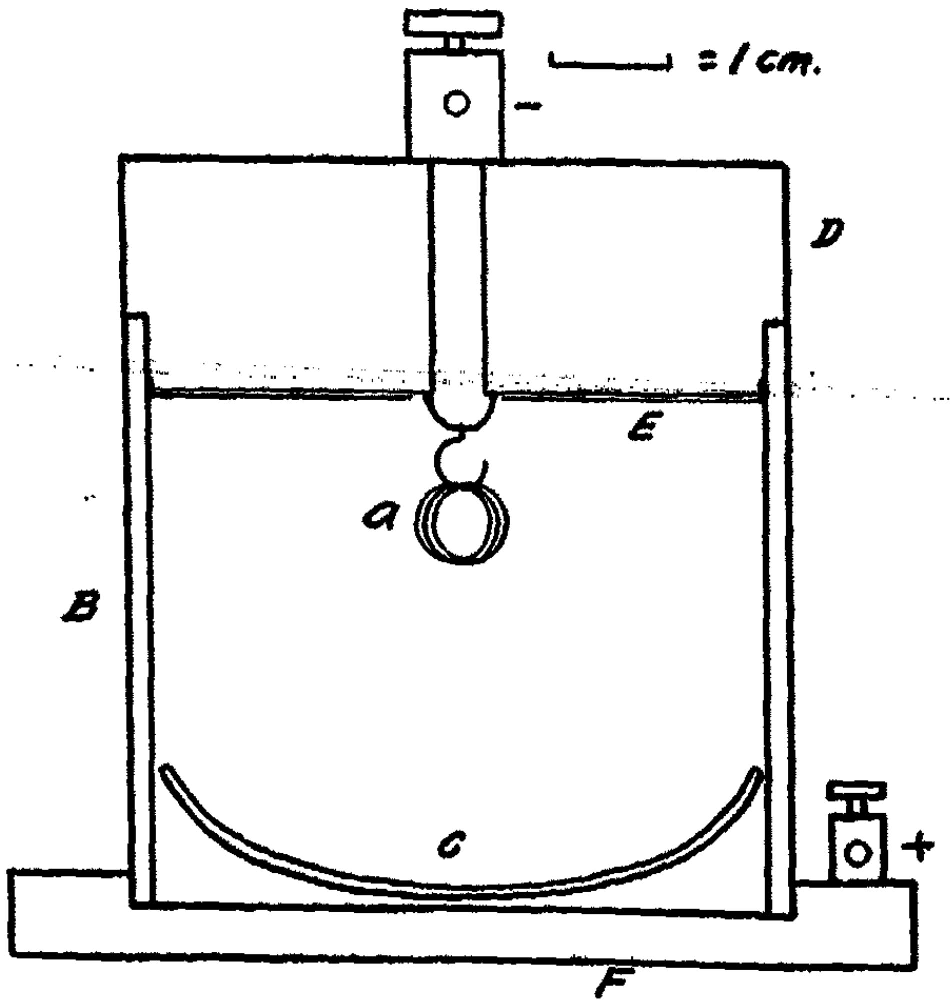

FIG. 1. EMANATION COLLECTOR

A, platinum loops; B, heavy brass cylinder; C, lead dish containing radiothorium preparation (the oxide or hydroxide); D, removable wood top; E, aluminum foil cut away around the binding post; F, brass base.

The electroscope

The beta ray electroscope used was purchased through Bender and Hobein of Munich.[3] An important aid in the measurements was an eyepiece scale consisting of vertical lines bisected by a horizontal line. The gold leaf could then be timed as it passed an intersection. All samples measured were in the form of thin salt layers on 6-cm. watch glasses of slight concavity and of uniform thickness. A special watch holder and guide held the sample in the same position under the aluminum window so that reproducible results were possible. It was found that the aluminum window (which was 0.07 mm. in thickness) needed to be larger than the watch glasses used because of the effect of the scattering of the beta particles. The scale of the electroscope was calibrated against the constant activity of a radioactive preparation. The natural fall of the electroscope was measured each day and this correction was made on the observed fall. To eliminate the "soaking in effect" of the insulation of the gold leaf system (an amber bead), which gives the gold leaf an abnormal natural fall after it has stood in a discharged condition for some time, the electroscope was charged up about an hour before using. The possible error due to this effect is illustrated by the following measurements:

Time elapsed since the electroscope was charged	*Natural fall of the gold leaf in scale divisions per minute*
10 minutes	0.71
34 minutes	0.63
1 hour, 3 minutes	0.51
1 hour, 43 minutes	0.50

The activities of all the samples of a set of measurements were calculated according to the disintegration formula back to the time of measurement of the first sample measured, t_0.

The acidity of the solutions

It has been observed that the acidity of the solutions plays an important part in the reproducibility of results in adsorbing radioactive ions on various materials. By controlling the acidity, the thorium B solutions could be diluted to any desired activity. For instance, two solutions of different activity were prepared and then the solution of higher activity was diluted with the calculated amount of acid to give the activity of the solution of lower activity. The measurements on both solutions are as follows:—

		Scale divisions per minute
A. Samples of solution of lower activity	1	106
	2	106
	3	107
B. Samples from the solution of higher activity after it had been diluted with the calculated amount of acid	1	111
	2	108

In another experiment 10 cc. of a solution which had an activity of 68.6 scale divisions per minute (when evaporated on a watch glass) was divided into two parts, and then 5 cc. of the solution was diluted with 5 cc. of acid. This 10 cc. when evaporated to dryness had an activity of 34.5 scale divisions per minute (calculated activity would be 34.3).

It was noted at the beginning of the measurements that there was an apparent adsorption of the radioactive material on the walls of the flasks and pipettes used in the measurements. It is known that glass is negatively charged against a neutral solution and that this negative charge decreases with increasing acidity of the solution. If the adsorption of the ions is due to the charge on the glass, this adsorption should decrease with increasing acidity of the solution.

A series of glass bottles containing an equal number of glass beads were prepared. Into each was pipetted 10 cc. of a radioactive solution and varying amounts of nitric acid and water to bring the total volume up to 25 cc. These bottles were then shaken and 10 cc. of the equilibrium solution was then withdrawn and evaporated to dryness on a watch glass; the activities of the deposits on the watch glasses were immediately measured. These activities were compared with the activity of the original solution and the per cent adsorption was computed. The data follows.

	Normality of acid	Per cent adsorption
1	0.004	66.4
2	0.004	64.7
3	0.044	61.8
4	0.044	61.6
5	0.084	60.6
6	0.084	61.2
7	0.125	58.6
8	0.125	59.2

The same series of experiments was carried out except that the activity measurements were made after the watch glasses had stood overnight (i.e., more than eight hours).

	Activity to t_0 in scale divisions per minute
Original solution	33.1
Original solution	32.6
Normality of acid	
0.0016	31.4
0.0097	33.3
0.0097	32.4
0.0179	33.4
0.0179	32.7
0.042	32.4
0.042	33.4
0.082	34.3
0.082	33.2
0.205	34.4
0.205	34.5
0.408	34.8
0.408	34.7
0.61	32.4
0.61	32.8

These two different series of experiments indicate that there is a selective adsorption of thorium C on the walls of the glass vessels and that the increase of acidity decreases this adsorption. In the case of any adsorption of thorium B, the increase of acidity in this experiment did not change the adsorption.

The results of a third series of experiments are given in figure 2. In this series of measurements the activity of the watch glasses was followed over a period of time. Curve A represents the activity of a solution pipetted out 30 minutes after t_0 and curve B represents the activity of the same solution from a sample pipetted out 3½ hours after t_0. Curve C represents the activity of the same solution after it had been shaken for 70 minutes in a soft glass bottle with glass beads and pipetted out 3½ hours after t_0. The final observations are given in table 1. From this data it is obvious that thorium B is not adsorbed by the glass. The normality of the acid used in this series of measurements was 0.0016. Comparing these curves with the theoretical ones (see page 665), it can be seen that there must have been a partial adsorption of thorium C on the walls of the pipettes and on the walls of the bottles.

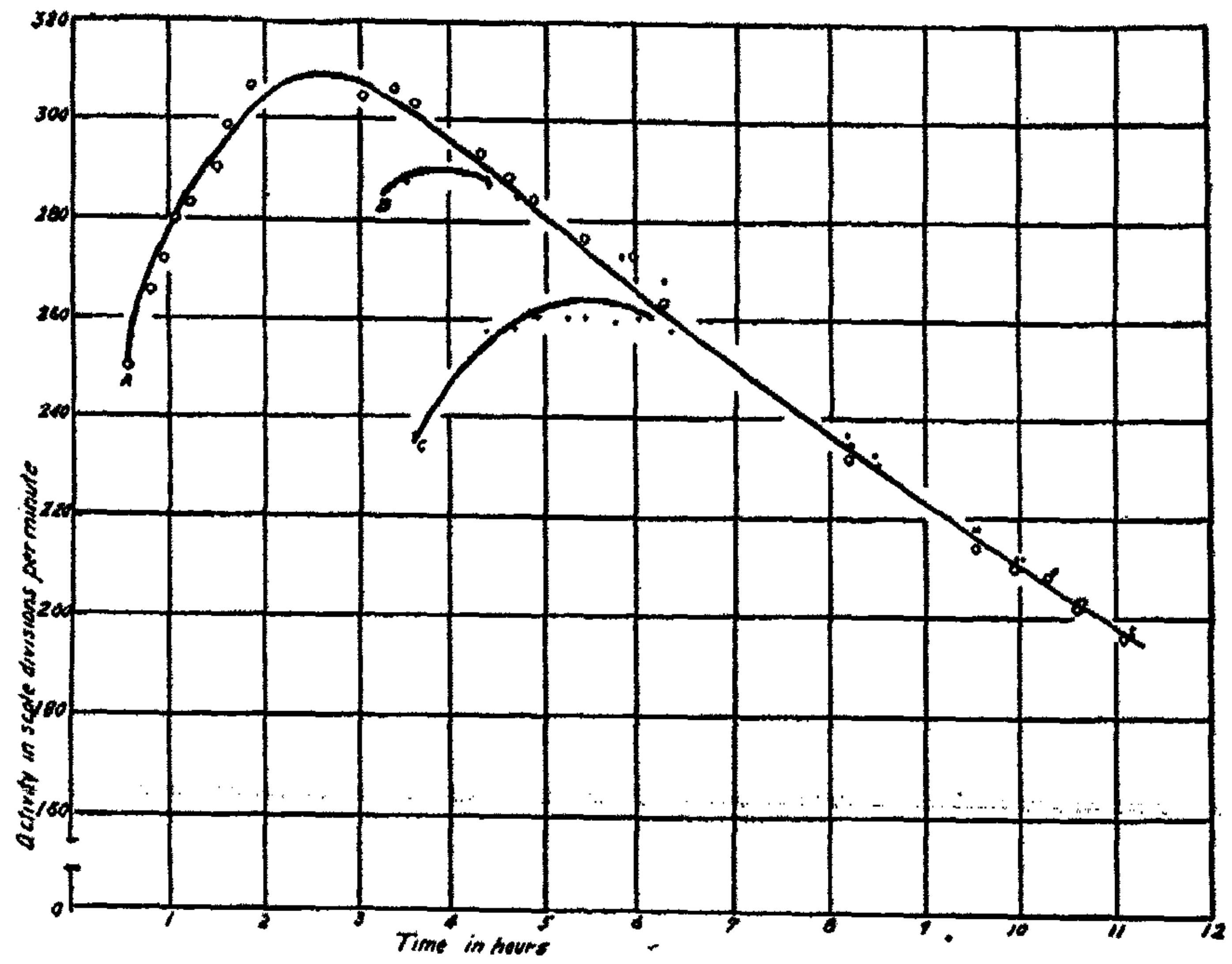

FIG. 2. ADSORPTION OF THORIUM C ON GLASS

TABLE 1

SOLUTION A		SOLUTION B		SOLUTION C	
TIME	ACTIVITY	TIME	ACTIVITY	TIME	ACTIVITY
hours	*scale divisions per minute*	*hours*	*scale divisions per minute*	*hours*	*scale divisions per minute*
3.02	306				
3.37	306				
3.58	303	3.53	288	3.65	236
4.33	292	4.37	288	4.38	257
4.63	288	4.67	286	4.68	259
4.88	283	4.92	278	4.95	260
5.17	278	5.18	278	5.22	260
5.38	276	5.42	270	5,43	260
5.75	273	5.77	273	5.78	259
5.98	273	6.00	268	6,03	260
6.28	263	6.30	268	6.35	257
8.17	231	8.18	234	8.20	236
8.47	231	8.48	232	8.52	230
9.55	214	9.58	218	9.62	218
9.95	210	9.98	212	10.02	212
10.32	207	10.35	210	10.35	208
10.65	202	10.68	204	10.72	204
11.10	196	11.15	197	11.18	198

Another experiment was carried out to determine the selective adsorption of glass for thorium C. A sample of 10 cc. of an active solution was allowed to stand on a clean watch glass for 20 minutes. The glass was then rinsed with distilled water, drained, and dried on a steam bath. The decay curve for the residue on the watch glass was then determined as accurately as the weakness of the activity of the residue would permit. The times and the $\log_e$ of the activities are given in table 2. These data are plotted in figure 3. The solid line is the theoretical decay curve for thorium C.

Thus it has been shown that in the handling of the radioactive solutions there is a selective adsorption of thorium C by the glass walls of the vessels used and that this adsorption is affected by the acidity of the solution.

Herta Leng (8) has made a study of the adsorption of thorium B and thorium C on filter paper, dialyzing tubes, different kinds of glass, and paraffin. We plotted a number of her results showing the relation between hydrogen-ion concentration and the amounts of thorium B and thorium C adsorbed on different kinds of glass. The results from these curves show:—

TABLE 2

TIME	$\log_e$ OF ACTIVITY
hours	
.50	1.55
.70	1.43
.93	1.35
1.10	1.24
1.53	1.01
1.78	.85
2.17	.73
2.43	.53

I. For thorium C (isotope of bismuth): (1) there is a maximum adsorption at a pH of from 5 to 7; (2) the adsorption drops off rapidly around a pH of from 2 to 3.

II. For thorium B (isotope of lead): (1) there is a maximum adsorption at a pH of about 9 to 10; (2) there is a sharp dropping-off of adsorption at a pH of about 7 to 8.

It has been suggested by a number of workers that thorium B, an isotope of lead, and thorium C, an isotope of bismuth, exist in solution both in the ionic and in the colloidal condition and that the equilibrium is determined by the hydrogen-ion concentration. It is easy to understand that the colloidal form of thorium C, bismuth oxysalt, could occur in a more acid solution than the colloidal form of thorium B, some basic salt of lead. Thus the effect of the acidity on the amount of adsorption would be caused by a change in (1) the charge on the glass and its attraction for a trivalent and a bivalent ion, and (2) the nature of the radioactive material in solution.

Hahn (9) calls attention to the colloidal nature of lead, thorium B, and bismuth, thorium C, in slightly acid solutions. According to the adsorption rule thallium (thorium C_2) would be more strongly adsorbed on silver bromide than lead and lead more than bismuth. In slightly acid solutions this adsorption is just the reverse, Bi > Pb > Tl. In neutral solution this difference is more pronounced. He explains this by the supposition that in slightly acid solution bismuth and lead do not exist as ions but as so-called "radiocolloids." These radiocolloids may consist of particles of dust, decomposition particles of glass, etc., which have adsorbed the products of hydrolysis of bismuth and lead salts and behave as true colloidal particles of bismuth (thorium C) and lead (thorium B). Hahn suggests that thorium

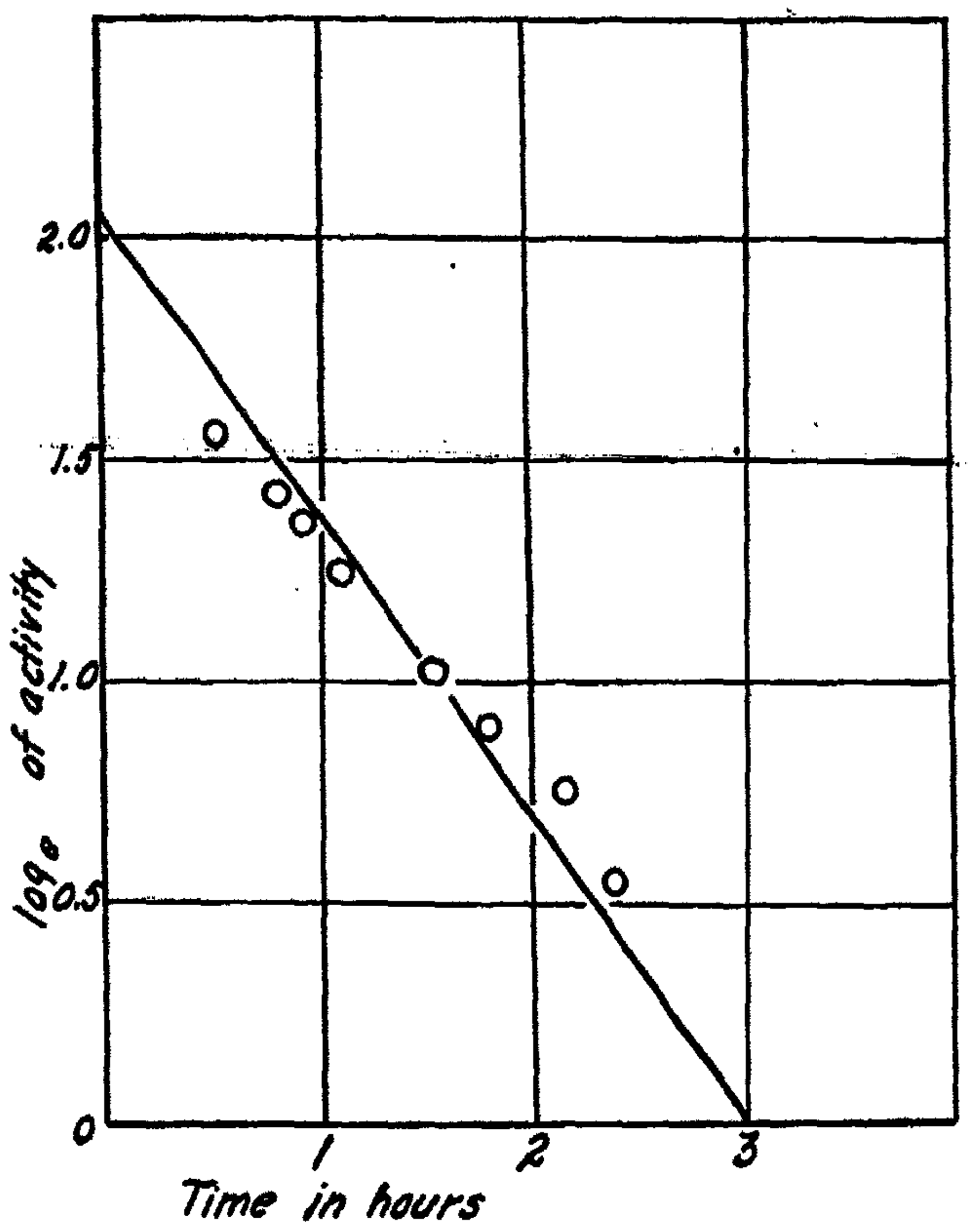

FIG. 3. DECAY CURVE FOR THORIUM C

B can be obtained in colloidal form or ionic form depending on the concentration of the acid used to dissolve it from the wire of the collector and also depending on the way that the solution is handled or diluted before adsorption is allowed to take place. He gives a series of experiments to show the possibility of the handling effect and suggests that this phenomenon warrants detailed study. The adsorption experiments take place in concentrations less than are usually considered necessary to exceed the solubility product of the salts concerned. The amount of adsorption would, in the case of these radiocolloids or pseudocolloids, depend on the number of ions in one of the particles of hydrolysis and the charge on the colloidal dust on glass decomposition particles. All of this would be a function of the hydrogen-ion concentration. The pseudocolloidal form of these two radioactive elements best explains the selective adsorption of thorium C, for it is not easy to explain this selective adsorption as due to the attraction of the negatively charged glass walls for the trivalent thorium C ion in preference to the divalent thorium B ion. Hahn was able to remove on a glass container the greater portion of the activity due to thorium B and thorium C by evaporating an active solution to dryness and then treating the residue with water.

In the following work on the adsorption of thorium B on the halides of silver and thallium, this effect was controlled by using sufficiently acid solutions to reduce this anomalous adsorption to a minimum.

SUMMARY

1. The technique used in the preparation and handling of the radioactive solutions used in the measurements in the two papers that are to follow has been described.

2. A study has been made of the selective adsorption of thorium C from a solution containing thorium B and thorium C on the walls of the glass vessels used in the work and the effect of the acidity of the solutions on this adsorption.

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PHASE RULE EQUILIBRIA OF ACID SOAPS. I

ANHYDROUS ACID POTASSIUM LAURATE

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The question of the existence or non-existence of acid soaps, analogous to the well-known acid sodium and potassium formates and acetates, has been in debate for the last one hundred and ten years (1). The latest authority (2) reviewing the subject concludes that they do not exist.

It is easy to obtain materials which have an empirical composition showing a simple integral ratio between soap and fatty acid, as, for example, by taking the sediment from a sufficiently dilute aqueous solution, or by mixing the components in the required proportion and crystallizing them out again together; but most writers have not found it necessary to apply the ordinary thermodynamic criteria for the existence of definite chemical compounds. Hence these materials are often regarded as mixtures, whether isomorphous or heterogeneous, or as "sorption compounds," especially since Donnan and White by extrapolation of their actual observations concluded that "the separation of the acid salt NaPa,HPa is extremely doubtful, although this composition has not been covered by the experimental data."

McBain and Stewart were the first to provide some proof that an acid soap KOl,HOl is a chemical entity, in that its composition does not vary when that of the mother liquor from which it is crystallized is altered over a fairly wide range. Many acid soaps have been prepared in beautifully crystalline form; their x-ray examination has been described by Piper. A series of phase rule diagrams was worked out at the University of Bristol, England, in the years 1925–1927 and this is the first installment of the results then obtained. They are conclusive with regard to the existence and constancy of composition of acid soaps as chemical compounds.

The acid soaps are important because they, and not the free fatty acids (which are too strongly dissociated), are the common products of hydrolysis in aqueous solution. In non-aqueous solvents they are far more soluble than ordinary soaps.

EXPERIMENTAL

Materials

Lauric acid (referred to as HL), Kahlbaum, melted at 44°C. Potassium laurate (referred to as KL), specially prepared by Kahlbaum, was the same as that used by McBain and Field (3).

The systems were prepared in thick-walled Duro glass tubes about 21 cm. in length and about 1.5 cm. in diameter, which were sealed after weighing the two components into them. They were then heated to whatever temperature was necessary to transform the contents into a single, homogeneous phase. Up to 180°C. this was done in a glycerol bath, and up to 400°C. in an electric oven made by winding nichrome wire around a hollow cylinder of sheet asbestos with two transparent mica windows. A thermometer was kept touching the side of the soap tube, and heating and cooling were carried out very slowly. Stirring was effected by slowly shaking the oven as a whole, avoiding the formation of air bubbles. Carefully standardized thermometers were used throughout the investigation. On cooling these systems down to room temperature, the separation of solid crystals took place in every case from the pure fatty acid up to a concentration of approximately 75 per cent KL, 25 per cent HL; systems containing more potassium laurate than this gave rise, on cooling the isotropic liquid, to anisotropic liquid crystals; on further cooling, these were followed at a somewhat lower temperature by solid crystals.

Method of visual observation

In every case the temperature, T_c, at which the last trace of solid crystal disappears upon very slow heating to give either an anisotropic or isotropic liquid, was observed. The results obtained in this manner were quite reproducible up to a concentration of 75 per cent KL but above this, owing to the cloudy nature of the liquid crystals formed, there was some doubt as to the exact temperature when the last trace of solid crystalline matter disappeared, and no satisfactory results could be obtained in this manner.

The upper boundary, T_i, between the liquid crystalline phase and the isotropic solution phase was obtained by cooling the homogeneous isotropic solution until it just went turbid; this denotes the presence of a second phase, which in this case was anisotropic liquid crystals. No supersaturation was observed to occur in the separation of the liquid crystalline phase; this is in harmony with the previous phase rule studies involving the separation of the anisotropic liquid (mesomorphous) state.

It will therefore be noted that from the mode in which T_c and T_i, respectively, are observed they are free from distortion due to possible supersaturation or undercooling and that they, therefore, constitute accurately determined points on the respective phase equilibrium boundaries.

TABLE 1

Visual observations of the temperature T_e at which the last trace of solid crystal disappears on heating, and of T'_i, the first temperature at which the homogeneous isotropic liquid becomes turbid or inhomogeneous on cooling

MOLE FRACTIONS		DESCRIPTION AT ROOM TEMPERATURE	T_e	T_i
KL	HL			
......	1.0000	White, waxy, crystalline mass	44.0	
0.0106	0.9894	White, waxy, crystalline mass	43.7	
0.0291	0.9709	White, waxy, crystalline mass	43.3	
0.0403	0.9517	White, waxy, crystalline mass	42.7	
0.0700	0.9300	Coarse, white, crystalline mass	41.0	
0.0919	0.9081	White, crystalline mass	43.5	
0.1330	0.8670	White, crystalline mass	52.6	
0.1663	0.8337	White, crystalline mass	57.0	
0.1972	0.8028	White, crystalline mass	63.9	
0.2266	0.7734	White, crystalline mass with traces of rod or needle acid soap crystals	69.0	
0.2269	0.7731	White, crystalline mass with traces of rod or needle acid soap crystals	69.2	
0.2492	0.7508	White, crystalline mass with traces of rod or needle acid soap crystals	74.3	
0.2818	0.7182	White, crystalline mass with traces of rod or needle acid soap crystals	80.0	
0.3310	0.6690	White, crystalline mass with traces of rod or needle acid soap crystals	85.5	
0.3604	0.6396	White, crystalline mass with traces of rod or needle acid soap crystals	89.7	
0.3977	0.6023	Yellowish white, crystalline mass with traces of rod or needle acid soap crystals	93.0	
0.4123	0.5877	Yellowish white, crystalline mass with traces of rod or needle acid soap crystals	107.1	
0.4203	0.5797	Straw-colored crystalline mass containing bunches of needle acid soap crystals radiating from a central nucleus	115.0	
0.4392	0.5608	Straw-colored crystalline mass containing bunches of needle acid soap crystals radiating from a central nucleus	125.0	
0.4655	0.5345	Straw-colored crystalline mass containing bunches of needle acid soap crystals radiating from a central nucleus	144.7	
0.4951	0.5049	Straw-colored crystalline mass containing bunches of needle acid soap crystals radiating from a central nucleus	160.0	

TABLE 1—*Concluded*

MOLE FRACTIONS		DESCRIPTION AT ROOM TEMPERATURE	T_e	T_i
KL	HL			
0.5386	0.4614	Straw-colored, powdery mass	185.0	
0.5694	0.4306	Straw-colored, powdery mass	200.5	
0.6170	0.3830	Straw-colored, powdery mass	211.5	
0.6419	0.3581	Straw-colored, powdery mass	217.5	
0.6658	0.3342	Straw-colored, powdery mass	226.0	
0.7155	0.2845	Straw-colored, powdery mass	235.5	
0.7515	0.2485	Straw-colored, powdery mass	?	259.5
0.7987	0.2013	Straw-colored, powdery mass	?	305.0
0.8569	0.1431	White, powdery mass	?	358.0
0.9234	0.0766	White, powdery mass	?	374.0
1.0000	0.0000	White, powdery mass	264.0	376.0

Results of visual observation

Table 1 describes the results that have been obtained in this manner, many of which have been checked by dilatometer observations (to be described later) and by microscope examination in the small stage furnace (also to be described later). The visual method proved quite satisfactory, giving reproducible results except near the lower eutectic, where either of the other two methods was more efficient.

The complete equilibrium diagram

Figure 1 is the complete phase rule diagram for the anhydrous two-component system, containing all the observations of table 1 together with those by the methods to be described in the sequel. The heterogeneous fields are marked by lightly drawn horizontal "tie lines" whose ends represent the phases in the mixture. The heavier horizontal lines mark the eutectic temperature, the transition temperature, and the lowest temperature at which the liquid crystalline soap phase appears.

First it will be seen that the isotropic liquid phase is completely delimited by the observations T_e and T_i. It embraces the upper half of the diagram above the melting points of the pure components. The melting point of lauric acid is lowered progressively to 40°C., the eutectic point, by addition of potassium laurate. The boundary of the liquid then rises to the transition point, 91.3°C. At all temperatures below 91.3°C. crystalline acid soap KL,HL separates as pure crystals either alone as in field A, or in heterogeneous mixture with crystalline KL on the left side of the diagram in field B, or in heterogeneous mixture with crystalline HL as in the field C. We shall see that there is no evidence for solid solutions or isomorphous mixtures.

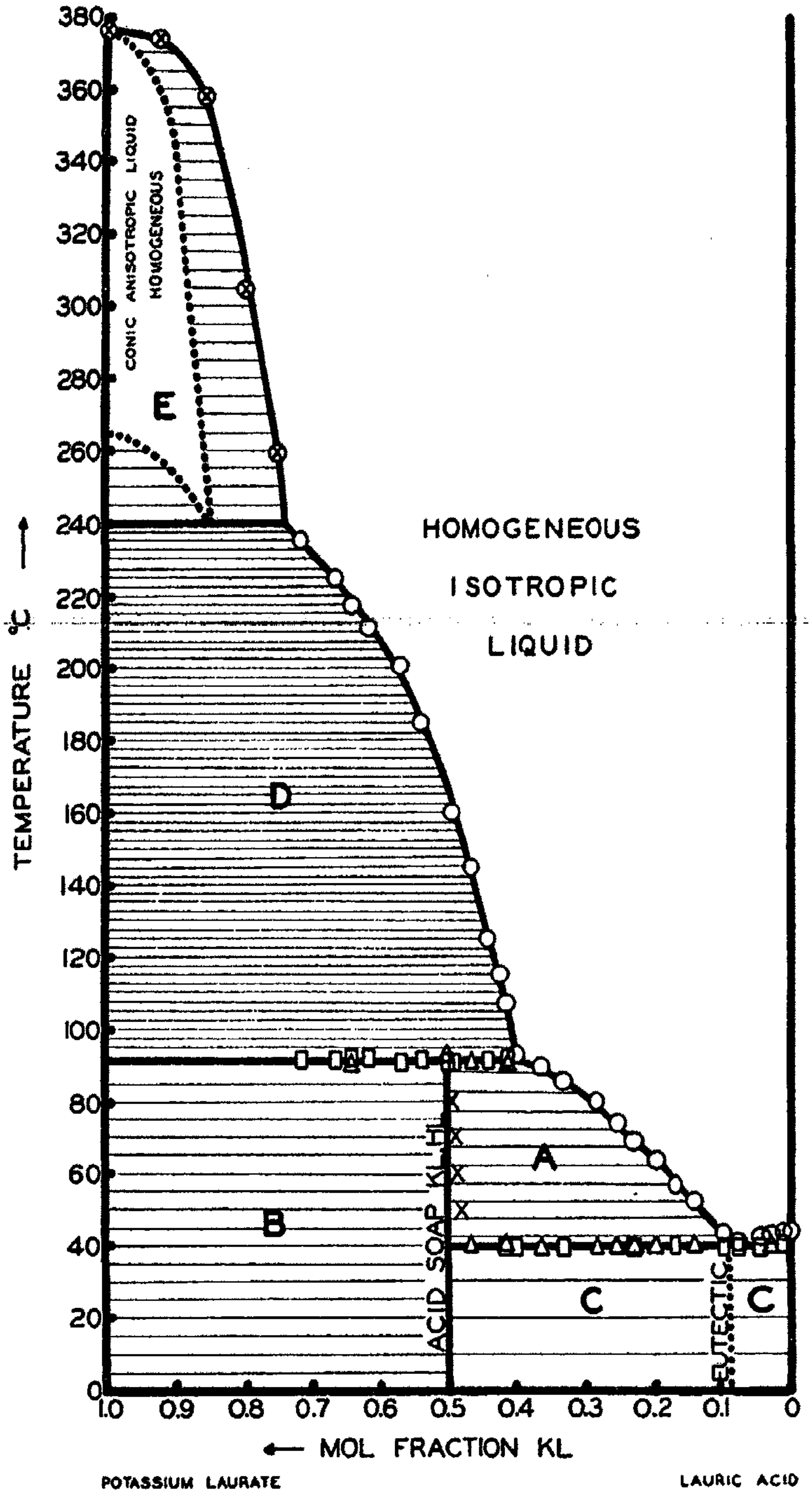

Fig. 1. The System Potassium Laurate–Lauric Acid

At 91.3°C., KL,HL exhibits a transition point, as shown also by the break in the boundary of the isotropic liquid, and breaks up completely into a mixture of that liquid with solid KL in field D. This transformation of KL,HL into liquid containing suspended KL is clearly visible. Therefore, no acid soap exists above 91.3°C. and the only one below 91.3°C. is KL,HL.

Another break in the isotropic liquid boundary is exhibited at 240°C., and inspection of the system shows that this is due to the appearance of the conic anisotropic liquid soap in field E. Whilst the boundaries of the isotropic liquid are exactly delimited even at the highest temperatures up to and including the final melting point, 376.0°C., of anhydrous liquid crystalline KL, the exact boundaries of field E have not been fixed. Above 376°C., KL and HL are completely miscible liquids.

The non-existence of isomorphous mixture and the existence of KL,HL

The extensively quoted and commonly accepted work of Donnan and White upon the anhydrous two-component system sodium palmitate–palmitic acid, alike through their imperfect method of separating liquid from solid phases and through their interpretation, has led to completely erroneous conclusions, not merely as to the position of some of the boundaries in the fragment of the diagram they chose for study, but also as to the very existence of isomorphous mixtures and of acid soaps themselves. The portion of the isotropic liquid boundary which they studied was, of course, correctly observed.

It therefore became necessary to scrutinize much more sharply the phase rule diagram just described and to obtain independent decisive evidence as to the truth of the interpretation given. Another communication will contain the complete phase rule diagram for anhydrous sodium palmitate–palmitic acid, showing the existence of two acid soaps, NaP,HP with a transition temperature of 74°C., and 2NaP,HP with a transition temperature at 91°C., and showing the non-existence of solid solutions or isomorphous mixtures in that system.

It is not easy to see with the naked eye the appearance of the first trace of liquid on heating the solid crystalline mass in field C, although the eutectic break at 40°C. is unmistakable, but progressively less distinct, as one approaches the composition KL,HL. We, therefore, turned to a dilatometric method of exhibiting the break at 40°C. which should occur at the upper boundary of the whole of the field C.

Dilatometric evidence for the absence of solid solutions

The design of the dilatometer, which was adopted after many trials, is given in figure 2. At the top of the diagram the dilatometer is exhibited in a horizontal position just after filling. This was done by attaching to a

Langmuir vacuum pump and a mercury reservoir with stopcock A closed and B open, then closing B and allowing mercury from the reservoir to fill the bulb and capillary as shown. The glass is cut at C and the position of the mercury meniscus adjusted with the dilatometer vertical, as in the lower figure, by heating the bulb to a temperature 20°C. higher than T_i

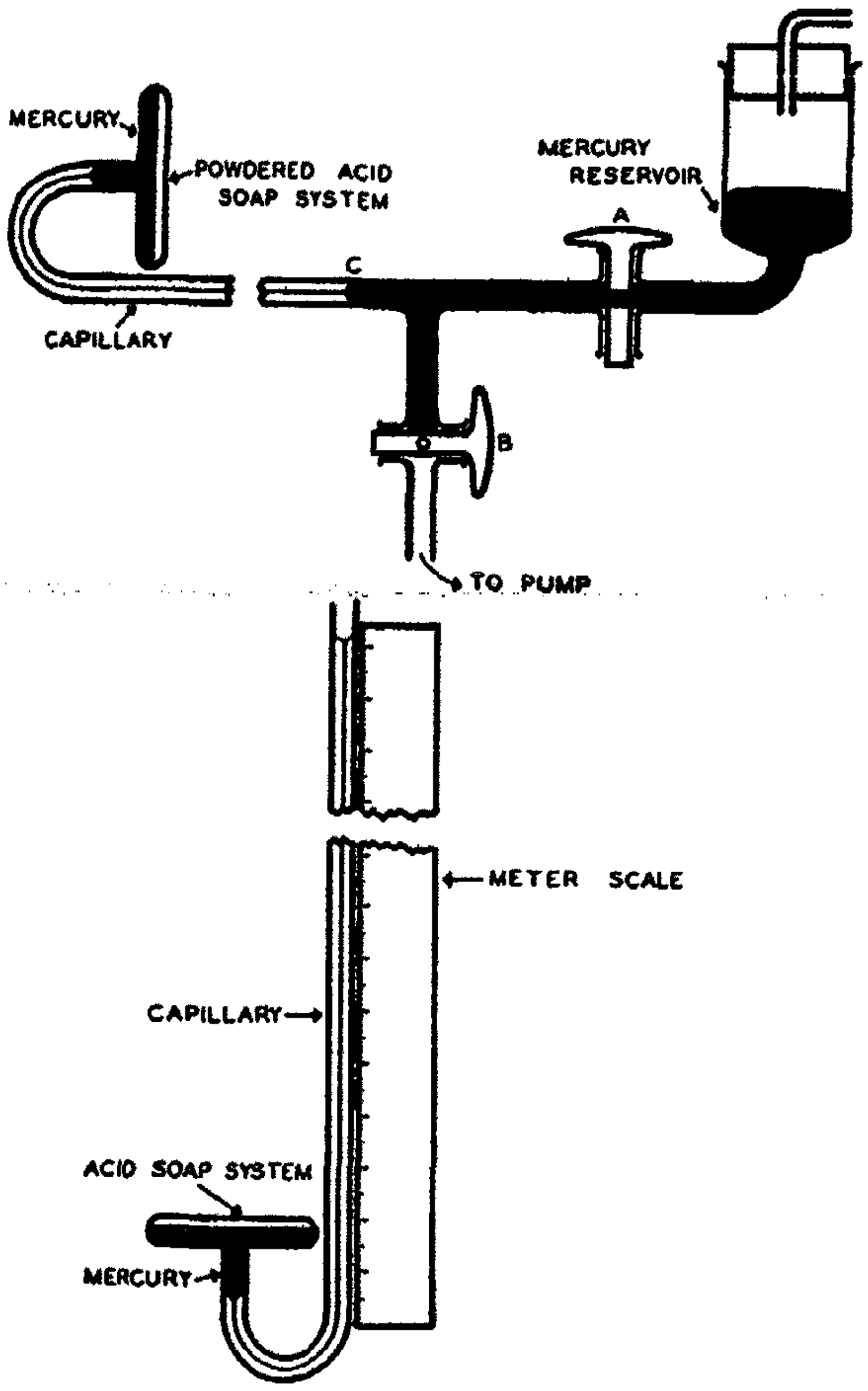

FIG. 2. DILATOMETER FOR OBSERVING CHANGES IN OR DISAPPEARANCE OF PHASES IN SYSTEMS OF LAURIC ACID WITH POTASSIUM LAURATE UP TO 0.72 MOLE FRACTION

at which the acid soap system becomes a homogeneous isotropic liquid, and then cooled to room temperature. Twenty dilatometers were placed in a thermostat and the expansion observed upon very slow heating (3°C. at a time, waiting twelve hours at each temperature before reading). In the neighborhood of an expected break, readings were taken at an interval of 1°C. A typical curve is given in figure 3. The break at 40°C. shows that the system contains eutectic mixture and is not a homogeneous solid solution. With one exception eutectic breaks for the nine systems occurred between 39.7°C. and 40.1°C. Where there was only 0.0106 KL the break was noted at 40.5°C. The dilatometer, therefore, proves that the system

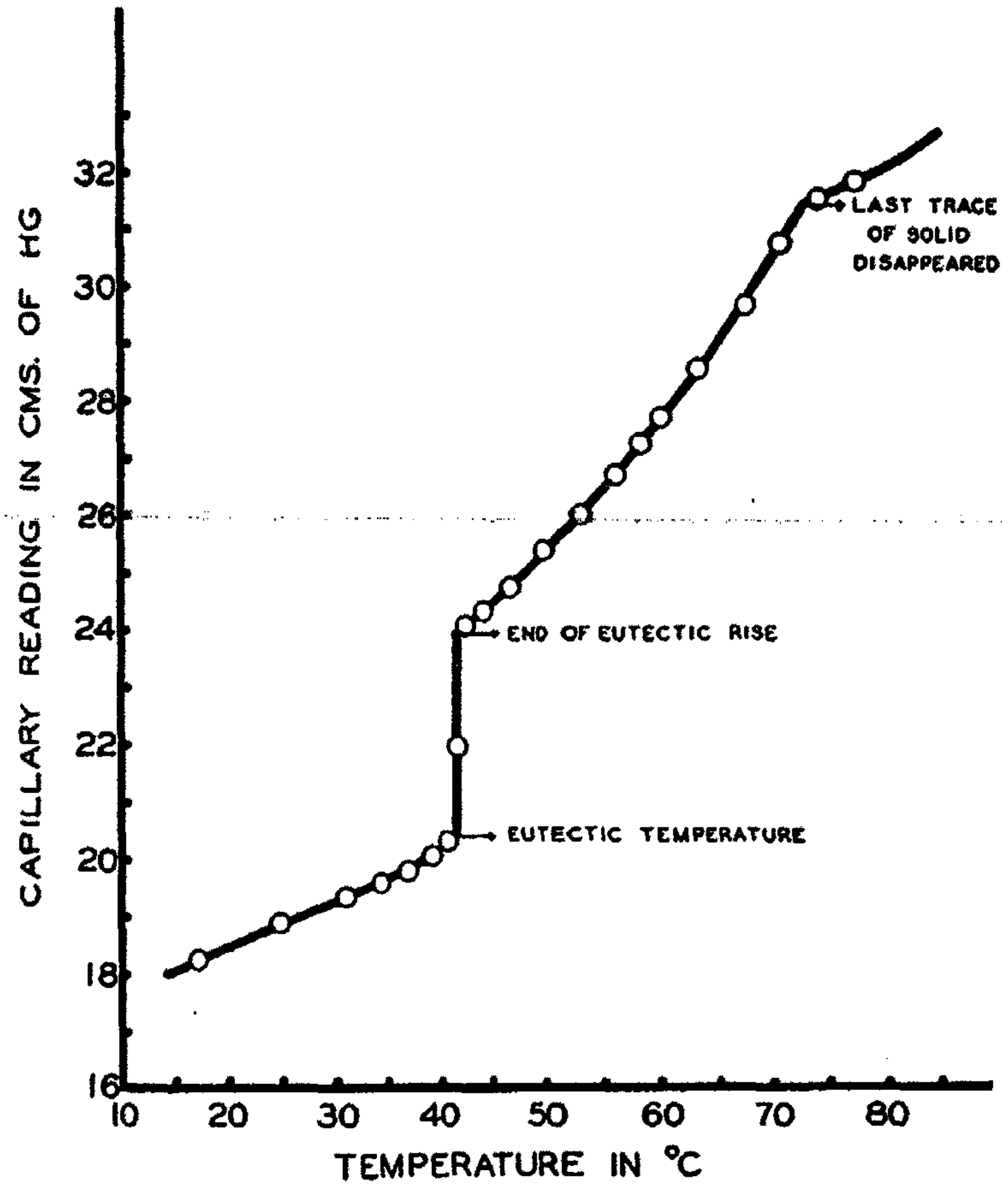

FIG. 3. DILATOMETER EXPANSION CURVE FOR A SYSTEM CONTAINING 0.773 MOLE LAURIC ACID AND 0.227 MOLE POTASSIUM LAURATE

Showing eutectic break at 40°C. and last trace of crystal disappearing at 72.5°C. (T_c).

is heterogeneous at least as far as 0.4 KL and somewhat beyond, although its indications necessarily become less distinct as the homogeneous crystalline phase KL,HL is approached.

The dilatometer for compositions containing more than 0.4 KL gives in each case a measure of the transition temperature at which the acid soap

KL, HL breaks up into its constituents. Ten readings lay between 90.5°C. and 91.5°C., confirming the interpretation of the break in the boundary of the isotropic liquid at 91.3°C.

Microscopic method

A thin layer of the powdered system between microscope slide and cover glass was examined between crossed Nicols, using an adjustable air thermostat upon the stage of the microscope. At room temperature all systems are doubly refracting, KL slightly and KL,HL strongly. The latter needle or rod-like crystals, therefore, appear very bright between crossed Nicols. On close examination the acid soap appears as elongated hexagonal plates often radiating from a point.

Upon slowly heating, the eutectic point is marked by the sudden appearance of isotropic liquid, black between crossed Nicols. As the temperature is progressively raised, the amount of isotropic liquid is seen by the proportion in which it fills the field. For example, for 0.029 KL + 0.971 HL the field became wholly black at 43.1°C., as compared with T_e = 43.3°C. observed with the naked eye. The first visible appearance of liquid in the nine systems occurred between 39.6°C. and 40.0°C., the temperature being sharply 39.8°C. for the most favorable compositions.

For the composition KL,HL, the system appears homogeneous, undergoing no visible change until 90.0°C., when the field suddenly darkens as the acid soap is transposed into slightly doubly refracting potassium laurate suspended in the isotropic liquid (black between crossed Nicols). On the other hand, when the mole fraction was 0.64 KL, the system was obviously heterogeneous, suddenly darkening at 89.9°C.

Screw press method

Donnan and White merely allowed liquid to drain away from solid matter, a process which is necessarily extremely incomplete. Here several systems in field A have been tested for heterogeneity by squeezing in a mild steel press lined with filter paper and with filter paper supported on fine mesh nickel gauze upon the perforated filter plate. The whole is maintained in the thermostat, and when the plunger is screwed down every three hours or so for several days, the isotropic oily liquid escapes. The residual hard white cake is analyzed by determination of T_e in a sealed glass tube, the composition being read off from figure 1. The composition of the cake lies close to KL, HL, showing that this is a separate pure phase. All systems heated above 91°C. yield a residue of pure KL in accordance with the results of the previous methods.

Others who have observed the acid soap KL, HL are Oudemans (1863), McBain and Eaton, Ekwall, etc. (*loc. cit.*), but this is the first time that it has been demonstrated that it is a pure chemical compound and the only one existing in this two-component system.

SUMMARY

It has been carefully demonstrated by a number of independent methods that the acid soap consisting of equal molecular proportions of potassium laurate and lauric acid is a true chemical individual that does not form solid solutions or isomorphous mixtures with either component. It exists only below 91.3°C., the transition temperature at which it decomposes into potassium laurate and the liquid mixture. There is a eutectic point between the acid soap and lauric acid at 40.0°C. and a break in the boundary of the isotropic liquid at 240°C., the lowest temperature at which anisotropic liquid exists in the two-component system.

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THE CATALYTIC ACTIVITY OF CHROMITES FOR THE OXIDATION OF CARBON MONOXIDE[1]

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The metal oxide and mixed metal oxide catalysts for the oxidation of carbon monoxide have received considerable attention since the investigations of Lamb, Bray, and Frazer (1). Bone (2) and his coworkers studied the oxidation of carbon monoxide using nickel, copper, and their oxides. Bennett (3) studied the activity of a number of purified oxides and found manganese, nickel, and cobalt oxides to be especially active at low temperatures. Recently Engelder and Miller (4) have shown that a mixed catalyst of titania and copper oxide was active, and Engelder and Blummer (5) have shown that a catalyst composed of cobaltic and ferric oxides has a high degree of activity in a temperature range of 0°C. to 200°C. Frazer (6) has shown that a catalyst composed of ferrous chromite is active at elevated temperatures.

This paper records the results of a continuation of work upon metal chromites as catalysts for the high temperature oxidation of carbon monoxide.

EXPERIMENTAL PART

Preparation of catalysts

The chromites were prepared by two methods, the method of Gerber (7) and the method of Lazier (8). The method of Gerber is as follows: A mole of the anhydrous metal chloride was ground with a mole of potassium dichromate to a fine powder. The mixture was fused in a porcelain dish at 900°C. for one hour. The resulting mass was leached with boiling water and concentrated hydrochloric acid, and then dried. It was found impossible to prepare cupric chromite by this method, as at 900°C. the cupric chromite decomposed forming cuprous chromite, which gradually reoxidized to cupric chromite upon cooling and yielded a mixture of cupric chromite and chromium oxide.

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[1] The material in this communication is abstracted from the dissertation submitted by E. C. Lory in partial fulfillment of the requirements for the degree of Doctor of Philosophy at The Johns Hopkins University, June, 1932.

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The method of Lazier consists of the preparation of a "metal ammonium chromate" and its subsequent decomposition, forming a mixture of the metal chromite and the metal oxide. The preparation of cobaltous chromite is given as an example. One mole of cobalt nitrate dissolved in 300 cc. of water was mixed with one mole of chromic trioxide in 100 cc. of water. The resulting solution was heated to 80°C. and to it was added three moles of ammonia. The resulting dark red precipitate was filtered by suction and washed sparingly with water and dried at 110°C. The dried precipitate was decomposed by heating small quantities in a casserole over a free flame. This gave an extremely fine greenish black powder composed of an equimolar mixture of cobalt oxide and cobaltous chromite. This was leached with concentrated hydrochloric acid until the acid gave no reaction for cobalt. The resulting chromite was a fine dark green powder.

Catalytic activity of chromites

The method used in testing the catalytic activity of the chromites for the oxidation of carbon monoxide consisted in the direct comparison between the catalyst and a catalyst known to be 100 per cent efficient. The apparatus and method developed by Bennett (3) was used with slight modifications. The dried gas mixture containing 1 per cent carbon monoxide was passed over the catalyst at the rate of 100 cc. per minute. The catalyst bed was 1 sq. cm. in area and 10 cm. deep. It was contained in a glass tube so arranged that the gases were preheated before passing over the catalyst. The carbon dioxide formed was removed by passing the gas through standard barium hydroxide. The remaining gases were dried and passed over hopcalite. This quantitatively oxidized any remaining carbon monoxide, the carbon dioxide formed being absorbed in a second absorption flask. The excess barium hydroxide in the two absorption flasks was titrated with standard oxalic acid. A direct comparison of the barium carbonate present in the two flasks gave the efficiency of the catalyst and was not affected by fluctuations in the rate of flow or concentration of carbon monoxide in the testing gas. With this method good checks were obtained with a similar catalyst at identical temperatures.

Table 1 gives the results of the tests upon the various chromites, giving the temperatures at which they possess 10, 20, 40, 60, 80, 90, and 100 per cent efficiency in the oxidation of a 1 per cent carbon monoxide–air mixture.

Surface oxidation of chromites

It has been noticed by O. G. Bennett that upon heating a chromite and washing with water, the filtrate was slightly colored. It was thought that this coloration might be due to the chromic acid formed by the oxidation of the chromite during heating. Tests were made upon copper, cobalt, and nickel chromites to determine if oxidation did occur and the extent of oxidation.

Experimental procedure. A 10-g. sample of the chromite was weighed into a Gooch crucible and leached with hot water until no test for chromic acid could be obtained in the filtrate. The crucible was then heated in an electric furnace to the desired temperature. It was leached with hot water in 200-cc. portions. The amount of chromic acid was determined iodometrically by titration with 0.01 *N* sodium thiosulfate. In most cases three to five leachings were required to remove completely the chromate present. The results of the surface oxidation on copper, cobalt, and nickel chromites are given in table 2, showing the temperature and time (in hours) of heating, with the per cent of CrO_3 by weight obtained in the filtrate.

These results tend to show that upon the heating of a chromite the surface of the chromite is oxidized to a chromate, but that the oxidation is only on the surface. To determine whether or not it was a case of equilibrium, a sample of copper chromite No. 3 was heated in a steel bomb at 400°C. under a pressure of 55 atmospheres of oxygen for twenty-four hours. Upon being leached it showed the same amount of chromate as when it was heated at atmospheric pressure.

Reduction of surface chromate by carbon monoxide

If the formation of chromate on the surface of a chromite is the active agent in the oxidation of carbon monoxide, the reduction of the chromate must occur at, or below, temperatures at which the chromite is catalytically active. Tests were carried out upon copper and cobalt chromites to determine whether or not the chromate present on the surface of the chromite was reduced by carbon monoxide.

The method of determining the reduction by carbon monoxide was to pass carbon monoxide over the chromite and absorb the carbon dioxide formed in standard barium hydroxide. Nitrogen was used to give an oxygen-free atmosphere.

Copper chromite No. 3. Reduction of the chromate and also of the copper oxide present took place at 100°C. The amount of carbon dioxide was in considerable excess of the amount of chromate present due to the simultaneous reduction of the copper oxide. Upon leaching after reduction no chromate was found to be present.

Cobalt chromite No. 1. Cobalt chromite was studied in more detail, as the cobalt oxide was not reduced by the carbon monoxide and quantitative checks of the amount of chromate present could be obtained. Reduction was observed when the temperature of the chromite reached approximately 160°C. Upon leaching with hot water a small amount of chromate was found to remain and not be reduced by the carbon monoxide at 200°C.

TABLE 1

Efficiency of catalysts used in the oxidation of a carbon monoxide–air mixture

CATALYST	TEMPERATURES (°C.) AT WHICH CATALYST HAS EFFICIENCY OF						
	10 per cent	20 per cent	40 per cent	60 per cent	80 per cent	90 per cent	100 per cent
Copper chromite[*]							
No. 1	30	31	33	35	46	61	94
No. 2	103	125	152	168	178	183	199
No. 3	44	57	74	91	118	120	142
No. 4	107	116	129	140	149	153	165
No. 5	55	78	82	84	85	87	102
Copper dichromate[†]							
No. 1	106	129	153	170	194	217	265
No. 2	217	239	273	300	327	341	357
Cobalt chromite[‡]							
No. 1	230	255	283	300	323	349	386
No. 2	66	84	100	100	101	104	111
No. 3	147	169	196	210	222	229	243
Ferrous chromite[§]							
No. 1	136	154	182	199	218	231	254
No. 2	216	239	248	270	304	400	—
Nickel chromite[¶]							
No. 1	259	283	320	353	383	398	431
Manganous chromite[‖]							
No. 1	235	259	285	298	313	341	420

[*] Copper chromite:

No. 1. Copper chromite prepared from "copper ammonium chromate," decomposed but not leached.

No. 2. Copper chromite from "copper ammonium chromate," leached with concentrated hydrochloric acid.

No. 3. Copper chromite from "copper ammonium chromate," leached with concentrated hydrochloric acid and heated to 700°C.

No. 4. Copper chromite No. 3 heated in a bomb for twenty-four hours at 400°C. under a pressure of 55 atmospheres of oxygen in the hope of increasing the oxidation of the chromite to chromate.

No. 5. Catalyst prepared by precipitation of cupric carbonate upon a sample of copper chromite No. 3. Heated to 170°C. for three hours with the carbon monoxide mixture passing over it, and then tested. No. 1 and No. 5 have nearly identical activities.

[†] Copper dichromate:

No. 1. Copper dichromate prepared by saturating a solution of chromic acid with basic copper carbonate and slowly evaporating at room temperature in a vacuum. Material heated to 250°C., cooled, and tested.

No. 2. Cupric dichromate, Eimer and Amend C. P. crystalline material, heated for eight hours at 150°C. and at 215°C. for six hours. Upon completion of testing, a Bunsen active oxygen test showed the presence of 76 per cent cupric dichromate.

‡ Cobalt chromite:
No. 1. Cobalt chromite prepared by Gerber's synthesis.
No. 2. Decomposition product of "cobalt ammonium chromate." Not leached.
No. 3. Cobalt chromite from "cobalt ammonium chromate," leached with concentrated hydrochloric acid until free of cobaltous oxide.

§ Ferrous chromite:
No. 1. Decomposition product of "ferric ammonium chromate." Not leached.
No. 2. Ferrous chromite prepared by Gerber's synthesis.

¶ Nickel chromite:
No. 1. Nickel chromite prepared by Gerber's synthesis.

‖ Manganous chromite:
No. 1. Manganous chromite prepared by Gerber's synthesis.

TABLE 2

Surface oxidation on copper, cobalt, and nickel chromites

TEMPERATURE	TIME	PER CENT CrO_3	TEMPERATURE	TIME	PER CENT CrO_3
Copper chromite No. 3					
Test No. 1			Test No. 2		
degrees C.	*hours*		*degrees C.*	*hours*	
200	10	0.0504	130	36	0.0100
450	1	0.0663	160	73	0.0212
330	10	0.0660	450	2	0.0651
300	2	0.0641	300	3	0.0663
300	16	0.0688	328	7	0.0693
100	250	0.0001	300	8	0.0664
Average for high values = 0.0678 per cent CrO_3					
Cobalt chromite No. 1					
Test No. 1			Test No. 2		
450	6	0.0728	300	18	0.0680
300	6	0.0623	500	5	0.0728
300	11	0.0720	530	5	0.0734
200	12	0.0332	900	6	0.0730
500	7	0.0730	160	1168	0.0102
Average for high values = 0.0738 per cent CrO_3					
Nickel chromite No. 1					
Test No. 1			Test No. 2		
430	5	0.0251	500	11	0.0256
460	5	0.0252	500	3	0.0240
410	3	0.0262	675	3	0.0241
400	84	0.0276	500	12	0.0236
530	73	0.0244	500	10	0.0262
800	3	0.0261	800	3	0.0253
Average for high values = 0.0260 per cent CrO_3					

The results of the reduction of cobalt chromite are given in table 3, giving the number of cubic centimeters of 0.01 N thiosulfate solution required to titrate the chromate present.

TABLE 3

Results of the reduction of cobalt chromite

TEST NO. 1		TEST NO. 2	
Chromate by leaching	22.61 cc.	Chromate by leaching	22.05 cc.
Chromate by reduction	23.33 cc.	Chromate by reduction	21.79 cc.
Chromate by reduction	22.81 cc.	Chromate by reduction	19.41 cc.

These results indicate that the chromate formed upon the surface of the chromite is reduced by carbon monoxide at the same temperatures at which the chromites become catalytically active.

Adsorption of DuPont Scarlet 2RL by chromites

Paneth and Vorwerk (9) have shown that Ponceau 2R is adsorbed on the surface of crystalline lead sulfate apparently in a monomolecular layer, and by adsorbing it on a surface of known area they have calculated the area occupied by one molecule of the dye when it is adsorbed upon the surface of lead sulfate. The adsorption of the dye upon copper, cobalt, and nickel chromites has been measured. In these experiments DuPont Scarlet 2RL was used, as it is the same dye chemically as Ponceau 2R.

TABLE 4

Adsorption of DuPont Scarlet 2RL upon chromites

CHROMITE	WEIGHT OF DYE ADSORBED BY 1 GRAM OF CHROMITE $\times 10^4$ GRAMS	MOLES OF DYE ADSORBED BY 1 GRAM OF CHROMITE $\times 10^7$	NUMBER OF MOLECULES OF DYE ADSORBED $\times 10^{-17}$	SPECIFIC SURFACE OF CHROMITES $\times 10^{-3}$ SQ. CM.
$CuCr_2O_4$	5.71	11.89	7.21	14.38
$CoCr_2O_4$	9.63	20.05	12.15	24.23
$NiCr_2O_4$	2.20	4.58	2.78	5.54

The method used was that of Paneth and Vorwerk. One and one-half grams of chromite was weighed into an ampoule of about 15 cc. capacity. Ten cubic centimeters of the dye solution was admitted with a pipette, the ampoule sealed, shaken for an hour and then centrifuged. Ten solutions of increasing concentration were used to obtain an adsorption isotherm at room temperature. Five cubic centimeters of the clear supernatant liquid was pipetted out and diluted to a dilution easily read upon the colorimeter. The comparison was made by means of a Bausch and

Lomb colorimeter. The results of the adsorptions of DuPont Scarlet 2RL upon the chromite are shown in table 4.

Owing to the high concentration of dye necessary to reach saturation of the surface and the attendant difficulties in determining the amount adsorbed, the results given in table 4 are not accurate to better than 10 per cent.

Combining the amount of surface found by dye adsorption with the amount of chromic acid found by leaching, the area occupied by each chromium atom can be calculated. The results are shown below.

	Area occupied by each chromium atom on the surface
Cobalt chromite	5.49×10^{-15} sq. cm.
Nickel chromite	3.52×10^{-15} sq. cm.
Copper chromite	3.50×10^{-15} sq. cm.

X-ray diffraction patterns were taken of cobalt, copper, and nickel chromites to determine whether or not the chromites prepared in this investigation were true chromites or mixtures of the oxides. Powder diagrams showed them to be definite compounds and not mixtures. Copper chromite was apparently not a cubic lattice and the x-ray investigation of this compound is being continued.

DISCUSSION

There are two possible explanations for the activity of the chromites in the oxidation of carbon monoxide: (1) the adsorption of the carbon monoxide with its activation through adsorption, or (2) the adsorption and activation of the oxygen. From the results of the surface oxidation of the chromites and the reduction of the chromate formed it would seem more logical that the activity is due to the adsorption of oxygen to form a chromate and its activation through a chemical formation. The activation of the saturated oxygen molecule would seem to be the more important factor, rather than the activation of the unsaturated carbon monoxide molecule.

The activity of the decomposition product of the "metal ammonium chromate" appears to be due to the presence of the metal oxide. When this mixture is leached with acid the oxide is removed, and the activity is then due to that of the chromite.

The oxidation of the chromites to chromate seems to be limited to a surface reaction, as increased heating under high pressure of oxygen did not increase the amount of chromate formed. The chromate appears to form a surface film that prevents further oxidation.

Studies of the adsorption of carbon monoxide, oxygen, and carbon dioxide by the chromite and chromate surfaces are now being carried out.

SUMMARY

1. The catalytic activity of copper, cobalt, nickel, manganous, and ferrous chromites for the oxidation of carbon monoxide has been determined.

2. It has been shown that upon heating the chromites are oxidized to sexivalent chromium on the surface, the surface film preventing further oxidation.

3. The chromate formed on the surface of the chromite is reduced by carbon monoxide at, or below, the temperatures of catalytic activity of the chromite for oxidation of carbon monoxide.

4. The specific surface of the chromites was determined by the method of Paneth and Vorwerk through adsorption of DuPont Scarlet 2RL.

5. An explanation of the activity of the chromites for the oxidation of carbon monoxide through the formation of a surface compound has been proposed.

The writer wishes to express here his appreciation to Professor J. C. W. Frazer, at whose suggestion and under whose supervision the work described was carried out.

He also wishes to thank Dr. O. G. Bennett for supplying him with a sample of ferrous chromite and for his helpful criticism during this investigation.

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THE SOLUBILITY OF THIOUREA IN WATER, METHANOL, AND ETHANOL

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INTRODUCTION

Solubility data on thiourea, an analogue of urea, in water is limited to a few isolated temperatures (4, 8, 11, 12). No previous determinations on the solubility of thiourea in water, in methanol, or in ethanol over a temperature range have been made. Such data are of some interest from the standpoint of a study of concentrated solutions—their ideality, non-ideality, and the like.

MATERIALS

The thiourea used was obtained from the Eastman Kodak Company and was their best grade. It was purified by recrystallization three times from water. The final product had a melting point of 181.4°C., which was slightly below that recorded in the literature (6).

A portion of the above thiourea was further purified by two recrystallizations from C.P. methanol. The final product showed a melting point of 181.4°C., which was the same as that of the sample after the third water recrystallization.

The purity of the thiourea was checked by chemical analysis for its sulfur, nitrogen, and thiourea content. It was felt that the data from analysis would be more reliable than the melting point determinations, because of the decomposition of thiourea at its melting point.

The first sample showed an average sulfur content of 42.10 per cent for twelve determinations (eight by a sodium peroxide oxidation (3), and four by a nitric acid-bromine oxidation (13, 19)), with maximum deviations from the average of 0.07 per cent. The second sample (methanol recrystallization) showed an average sulfur content of 42.14 ± 0.04 per cent for three determinations (3). The nitrogen content of the thiourea samples, determined by the Gunning method (2) showed 36.79 ± 0.03 and 30.80 ± 0.2 per cent. The thiourea content, determined by the method employed by Kappana (7) as recommended by Reynolds and Werner (14) and modified by Werner (21), showed 99.97 ± 0.04 per cent and 99.98 ± 0.02 per cent for the water-recrystallized and methanol-recrystallized samples.

Boiled distilled water was employed in all determinations where water was the solvent. Baker's C. P. absolute methanol was twice refluxed with lime for six hours and then distilled through a six-bulb Le Bel-Henninger column. That portion boiling within 64.63 ± 0.01°C. (corr.) was collected and used in the solubility determinations. Pure grain alcohol was twice refluxed with lime for over six hours and distilled as under methanol. The distillate boiling within 78.43 ± 0.02°C. (corr.) was collected and used for the solubility determinations. The procedure for ethanol was essentially that of Merriman (9).

PROCEDURE AND APPARATUS

The synthetic method of Alexejew (1) was employed in making the solubility determinations. This method consisted in heating weighed quantities of solvent and solute in a sealed tube, rotated in a water bath, and noting the temperature at which the solid phase had nearly disappeared. In recent years other investigators (16, 17, 18, 20) have found this method to be accurate and a reliable means for determining the solubility of solids in various solvents. As pointed out by these investigators, care must be taken in attaining true equilibrium conditions at the solubility temperature; this can ordinarily be obtained through slow heating and using low rates of temperature rise. A temperature rise of 0.01°C. per minute was used in some cases, though in many cases thermostating for a period of time was employed. Sunier (17) pointed out that with a rate of heating of 0.01°C. per minute, results well within 0.1°C. of the true solubility temperature were obtained for naphthalene in aliphatic alcohol systems. The author feels that this same degree of accuracy would hold for the systems studied in the present research.

The results obtained by the synthetic method are necessarily under different pressures. This question has been given extensive theoretical and practical consideration. Although it is possible that extremely high pressures would exert an influence, statements (15) are found that under ordinary conditions in which the pressure does not exceed ten atmospheres, no noticeable effect on solubility would be produced. No abnormalities in the solubility curves obtained by this method have been attributed to variation in pressure. The apparatus used has been described earlier (17).

Other investigators (16, 17, 18, 20) have shown that the size of the crystal is of importance in attaining true equilibrium conditions. The method was that ordinarily employed and consisted in rapidly heating the tube to a temperature where all the solute dissolved, and then cooling rapidly with vigorous shaking.

Thin wall Pyrex tubes of 7 mm. internal diameter and approximately 14 cm. long were used. The tubes were cleaned with sulfuric–chromic acid cleaning solution, rinsed with distilled water, and then heated over an open

Bunsen burner to dull redness, placed in a desiccator, allowed to cool, and weighed. For marking the respective tubes, they were first coated with paraffin, the desired identification marks inscribed with a steel pen, and hydrofluoric acid (48 per cent) added. After five minutes, the paraffin was dissolved off with acetone, and the tube prepared as described above.

In these determinations a thermometer certified by the Bureau of Standards was employed. The thermometer could be read to ± 0.01°C. with the aid of a magnifying glass. The temperatures recorded should be accurate to ±0.02°C.

Some preliminary data was obtained for the possible decomposition of thiourea in water solutions. The respective samples of these materials were heated with water at 100°C. for two hours and then tested for ammonium thiocyanate. It was found that the thiourea sample showed an absence of ammonium thiocyanate, indicating that under these conditions no conversion had taken place.

TABLE 1

Solubility of thiourea (recrystallized from water) in water

THIOUREA	SOLVENT	THIOUREA	THIOUREA	SOLUBILITY TEMPERATURE
grams	*grams*	*weight per cent*	*mol fraction*	*degrees C.*
0.2968	2.9993	9.0	0.0229	12.43
0.4050	2.9543	12.06	0.0314	19.88
0.5113	2.9899	14.60	0.0389	25.11
0.6369	2.9550	17.73	0.0486	30.38
0.7855	2.9862	20.83	0.0586	35.23
1.2715	1.9846	39.05	0.1317	57.05
0.9010	3.0165	23.00	0.0658	38.31
1.1094	2.8897	27.74	0.0833	44.30
1.2975	2.9727	30.38	0.0937	47.34
1.0700	1.9636	35.27	0.1143	53.02
1.5590	1.9423	44.53	0.1598	62.85
1.8848	1.9927	48.61	0.1829	67.43
1.9197	1.5217	55.78	0.2299	75.96
2.2502	1.5084	59.87	0.2610	81.28

EXPERIMENTAL RESULTS

The results of the various thiourea solubility determinations are presented in tables 1 and 2. Concentrations have been calculated and tabulated on both the mol fraction and weight per cent basis. The data were plotted on a large scale according to the method of Hildebrand and Jenks (5), as the log N_2 versus 1000/T. The solubilities at rounded temperatures were read off and are given in table 3.

TABLE 2

Solubility of thiourea (recrystallized from water and methanol)

THIOUREA	SOLVENT	THIOUREA	THIOUREA	SOLUBILITY TEMPERATURE
Solubility in water				
grams	*grams*	*weight per cent*	*mol fraction*	*degrees C.*
0.5199	2.9260	15.09	0.0404	25.90
0.4905	2.7676	15.05	0.0402	26.02
0.9347	2.6717	25.92	0.0766	42.00
1.0462	2.8386	26.93	0.0800	43.11
1.9521	1.9358	50.21	0.1925	69.26
Solubility in methanol				
0.2101	1.5484	11.95	0.0540	25.11
0.3108	1.5879	16.37	0.0760	40.80
0.4064	1.5409	22.01	0.0999	53.76
0.5046	1.5500	24.56	0.1205	62.00
Solubility in ethanol				
0.0864	2.3103	3.61	0.0221	20.25
0.1107	2.2510	4.69	0.0289	31.99
0.0873	1.5303	5.40	0.0334	37.69
0.1426	2.1111	6.33	0.0393	45.14
0.1465	1.8861	7.21	0.0449	51.22
0.2135	2.3031	8.48	0.0531	58.05
0.2457	2.2585	9.81	0.0618	64.77

TABLE 3

Solubility of thiourea in water and alcohols at rounded temperatures

(Expressed in mol fractions of thiourea)

TEMPERATURE	WATER	METHANOL	ETHANOL
degrees C.			
20	0.0314	0.0481	0.0220
25	0.0389	0.0539	0.0247
30	0.0478	0.0603	0.0277
35	0.0583	0.0673	0.0312
40	0.0707	0.0748	0.0349
45	0.0856	0.0833	0.0392
50	0.1023	0.0922	0.0438
55	0.1221	0.1025	0.0492
60	0.1450	0.1150	0.0554
65	0.1700	0.1292	0.0622
70	0.1968	0.1452	0.0701
75	0.2243	......	......
80	0.2533	......	......
85	0.2860	......	......

DISCUSSION OF RESULTS

The results of the solubility determinations in water were compared with those published by earlier workers. Dehn (4), some years ago, made a single qualitative determination of the solubility of thiourea in water at a temperature of 20°C. to 25°C. This result, as the author states, is not of a high degree of accuracy. Kettner (8) somewhat later determined the solubility of thiourea in water over a temperature range of 0°C. to 145°C. His determinations were made at 0°, 50°, 56.5°, 97.2°, 120.6°, and 145°C. Hence, comparison with the author's data could be made at two points only, viz., 50°C. and 56.5°C. These determinations show some variance from the results obtained in the present research, especially the value at 50°C. Oliveri-Mandala (11, 12) more recently determined the solubility of thiourea in water at temperatures from 10°C. to 25°C. The results at 20°C. and 25°C. when compared to the present research show considerable variation, especially the value at 25°C. The results of the above-mentioned investigators are compared in graphic form with the author's work in figure 1, where the data are plotted according to the method of Hildebrand and Jenks (5). Over a temperature range of 20°C. to 60°C., it is found that a straight line results; above 60°C. departure from the straight-line function increases and becomes greatest at the higher temperatures.

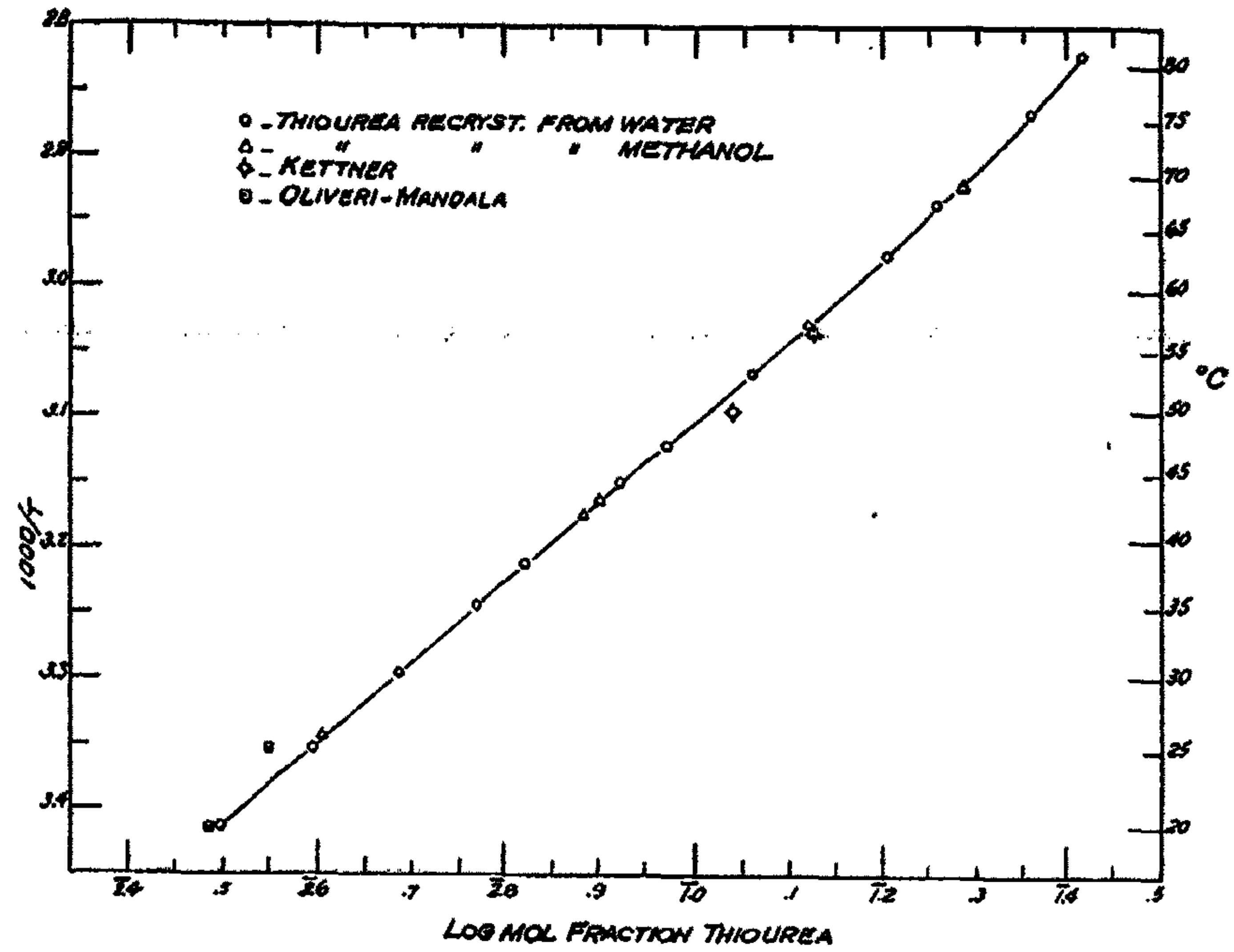

FIG. 1. SOLUBILITY OF THIOUREA IN WATER

Data for a sample of thiourea recrystallized from water and methanol are also presented. Here it is observed that the solubility determinations coincide with those already determined on the sample recrystallized from water only. It is thus apparent that the solubility of thiourea was not affected by the nature of the solvent from which it was recrystallized. A study of tables 1 and 2 shows the deviation obtained relative to the solubility of thiourea on the two samples used, viz., that recrystallized from water and that recrystallized from water and methanol. The fact that the results on the solubility determinations of the two samples of thiourea show such close agreement leads to the conclusion that these determinations are more accurate than those of previous published work.

It is felt that the foregoing results are accurate to well within ± 0.1°C. of the true solubility temperature. This figure represents the maximum deviation, whereas some of the determinations deviate much less. Between the temperature of 20°C. to 60°C., where the straight-line function exists, the mean deviation in solubility temperature for both samples of thiourea used was 0.07°C. It is believed that the solubility results obtained with both samples are of the same degree of accuracy. For that reason no distinction in the final results is made. The values of the solubility of the respective samples of thiourea were read off from the large plot previously referred to. From this plot the equation of the straight line was determined, and found to be $\log_{10} N = -1621.6\ (1/T) + 4.029$. This is valid over the temperature range 20°C. to 60°C. It gives results to within one part per thousand of the values obtained from the plot.

The fact that the log N versus $1/T$ curve is a stright line over the temperature range of 20°C. to 60°C. leads one to inquire whether or not ideal solutions are encountered in this range of temperature. To attempt to extrapolate $\log N = 0$ is difficult, because it is known that above 60°C. the solubility of thiourea departs from a straight-line function, with increasing rapidity as the temperature is elevated. However when Kettner's (8) data at higher temperatures are plotted with those of the author, a smooth curve results and on extrapolation the curve almost intersects at the absolute melting point, i.e., where $\log N = 0$. The shape of the curve indicates that a reverse S form of curve discussed by Mortimer (10) is not formed. No data seems to be available concerning the latent heat and fusion of thiourea (no doubt because of the molecular transformation at its melting point). Hence, a comparison of the experimental and ideal shape of the line was not possible. It may be said that when the slope, 1621.6 (assumed to be constant over the entire range, which is not true to the fact) is multiplied by 4.583, a value of approximately 7400 calories is obtained. If the solution were ideal, this value would represent the latent mol heat of fusion of thiourea.

To determine further whether or not ideal solutions were formed by thiourea in water, a search for vapor pressure data was made. Apparently no data on the vapor pressure of thiourea in water solutions is available. Hence no comparison or calculation can be made to determine whether or not deviation from Raoult's law exists.

The solubility results of thiourea in methanol and in ethanol are found in table 2. These results are also presented in graphic form in figure 2. It is observed that between the temperature range of 20°C. to 70°C., thiourea in methanol and ethanol does not form a straight line when plotted according to the method of Hildebrand and Jenks (5). One would expect from the nature and chemical constitution of thiourea that it would be readily soluble in water, less soluble in methanol, and least soluble in ethanol. However, this is not the case. An unexpected phenomenon occurs, as shown in figure 2. The curves of the solubility of thiourea in water and methanol cross at about 43°C., i.e., at temperatures below 43°C. thiourea is more soluble in methanol than in water, and at temperatures above that point is more soluble in water than in methanol, when expressed on the mol fraction basis. The exact point where thiourea in methanol crosses the thiourea and water curve is where the mol fraction is equal to 0.08017, which is equivalent to a temperature of 43.24°C.

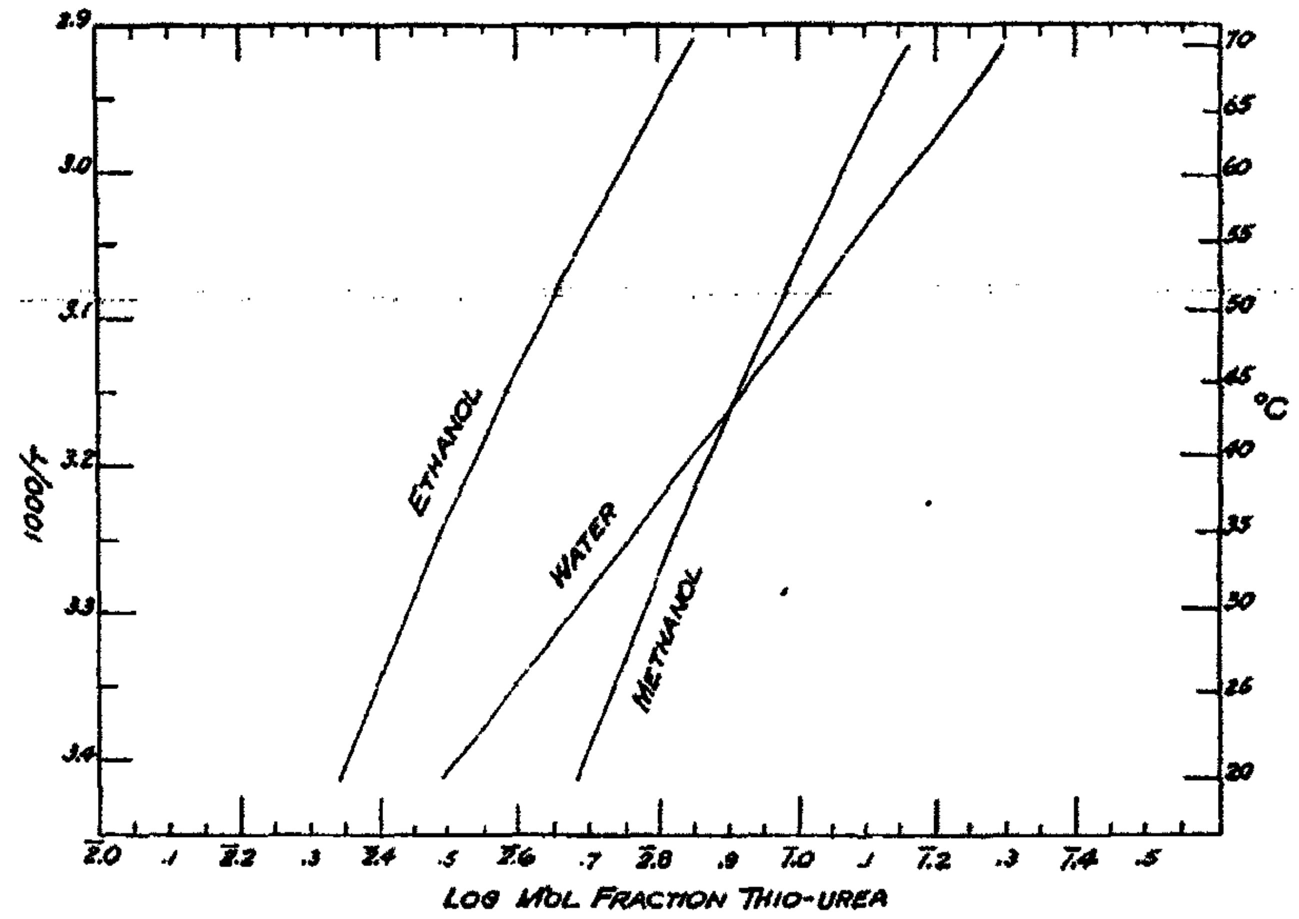

FIG. 2. SOLUBILITY OF THIOUREA IN WATER, IN METHANOL, AND IN ETHANOL

The solubility of thiourea in ethanol is as would be expected, viz., less than in water or methanol. No previous determinations on the solubility of thiourea in water, in methanol, or in ethanol over the temperature range studied have been made.

SUMMARY

1. Two samples of thiourea have been carefully purified and analyzed.

2. Nineteen determinations of the solubility of thiourea in water have been made, using the synthetic method in the temperature interval 15°C. to 80°C.; the precision in these runs is much higher than any previously published. The data may be accurately represented by the equation

$$\log_{10} N = -1621.6\ (1/T) + 4.029$$

in the temperature interval 20°C. to 60°C.

3. The solubility of thiourea in methanol and ethanol has been determined by the synthetic method from 20°C. to 70°C.

The author wishes to express his gratitude to Prof. A. A. Sunier for his interest and advice during the progress of this work, and to the Rochester Gas and Electric Corporation for the use of their equipment.

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ON THE EBULLIOSCOPIC METHOD FOR DETERMINING THE EQUILIBRIUM CONSTANT OF ESTERIFICATION

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A method of determining the so-called equilibrium constant of esterification by ebullioscopic measurements has previously been described (1). In the present investigation, a new ebullioscopic apparatus was used and some improvements and simplifications introduced in the technique.

It is clear that the boiling points of two reacting mixtures, the first one containing say 1 mole of ethyl alcohol and 1 mole of acetic acid, and the other 1 mole of ethyl acetate and 1 mole of water, differ considerably at the beginning of the reaction. The boiling temperatures, however, approach each other as the mixtures tend towards the equilibrium state. We may consider that equilibrium is established when the two mixtures boil at the same temperature. The composition of the two mixtures which must be identical is determined in order to calculate the equilibrium constant.

Previous experiments, with mixtures of the reacting substances in molar proportions, showed that it was not easy to get identical values for the boiling points of the two mixtures undergoing changes in opposite directions. Jozefowicz obtained a difference of 0.1°C., whilst Miss Blaszkowska succeeded in reducing the difference to 0.04°C. In the latter case the boiling point of the equilibrium mixture could be extrapolated with an approximation of 0.010°C. These relatively small differences could be due either to errors in the ebullioscopic measurements or to the very small velocity of reaction in the neighborhood of the equilibrium state.

The exact determination of the boiling point of a mixture containing volatile liquids is complicated by the fact that the volatile parts of the mixture evaporate and accumulate in the dead space of the ebullioscopic apparatus; this may cause differences in the measurements. On the other hand, the velocity of reaction may decrease to such a degree that the equilibrium and the equalization of the boiling points of the two mixtures might perhaps never be reached in practice. In order to investigate the cause of the phenomenon, the conditions governing ebullioscopic measurements have been improved. A new ebullioscopic apparatus suitable for investigating mixtures of volatile substances (2) and provided with a stop-cock in order to determine the correction for the dead space of the apparatus has been constructed. The new apparatus is shown in figure 1. The test tube sealed to the part B is immersed in the boiling liquid. This test tube is filled with mercury, into which the bulb of the thermometer dips. The temperature read on the thermometer does not correspond to the true boiling point on account of the overheating of the liquid, a correction for which can, however, be introduced without difficulty (3). In measurements of boiling points it is very important to obtain in both pieces of ebullioscopic apparatus an equal intensity of boiling. For this purpose they are provided with drop-counters, *f*. The intensity of the heating is regulated in such a manner that the number of drops flowing from the condenser D through the tube F is equal for both mixtures, reacting in opposite directions.

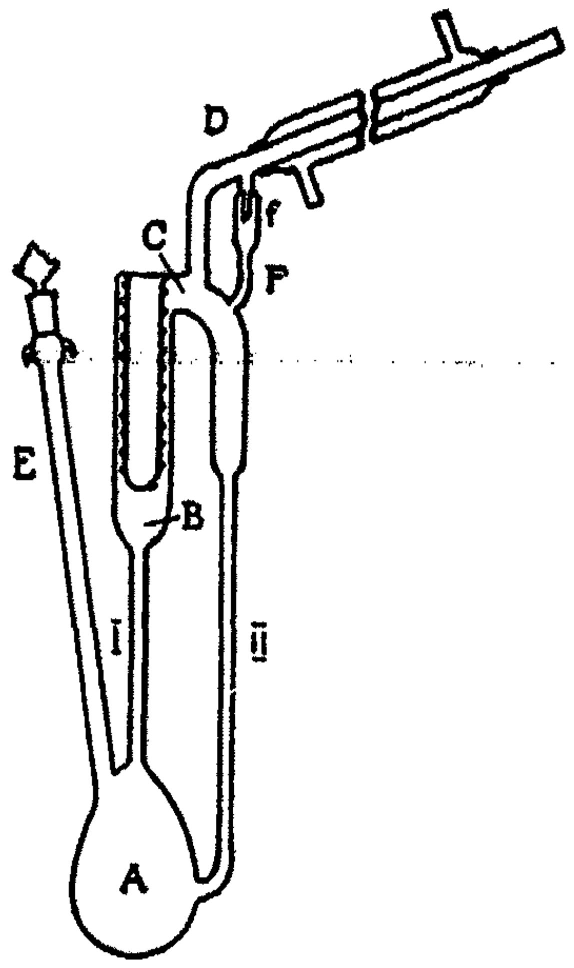

Fig. 1

ESTABLISHMENT OF THE EQUILIBRIUM AND DETERMINATION OF THE BOILING POINTS

The arrangement of the apparatus is shown in figure 2. The two ebullioscopes, A and B, each filled with one of the two mixtures undergoing changes in opposite directions, are connected by means of stop-cocks 1 and 2 with a manostat E of 3 to 4 liters capacity. The stop-cock 5 allows us either to fill the apparatus with nitrogen or to connect it with the atmosphere.

During the first part of the experiment (lasting several weeks) two other ebullioscopes, C and D, remain empty and the stop-cocks 3 and 4 are closed. The experiment is started by filling the whole apparatus with nitrogen. Then A and B are filled with the two mixtures. The stop-cock 5 is then closed and the bulbs of both ebullioscopes heated until the liquids begin to boil. The stop-cocks 1 and 2 are then opened. After having established a rate of equal boiling, measurements of the boiling points of the mixtures are started. For this purpose only one thermometer with an arbitrary scale is used, and it is carried over several times from one test tube to the other in order to eliminate the influence of the pressure changes in the whole apparatus. After measuring the difference of the boiling points, $\Delta t = t_A - t_B$, the stop-cocks 1 and 2 are closed and the boiling of the mixtures maintained for several days. The measurement is repeated by opening each time the stop-cocks 1 and 2. When, for example, the formation of ethyl acetate is investigated, it is possible to fill the ebullioscopes with mixtures which are quite near to the equilibrium state, for instance, which differ in their boiling points by not more than 0.300°C., or even 0.060°C. The realization of practically identical boiling points for both liquids, within 0.001°–0.003°C., requires four to nine weeks. In some cases, when impurities were probably present or when the one-sided evaporation produced a little difference in the composition of the two liquids, we noted a greater difference. As is shown in the table, Δt did not, however, exceed 0.010°C.

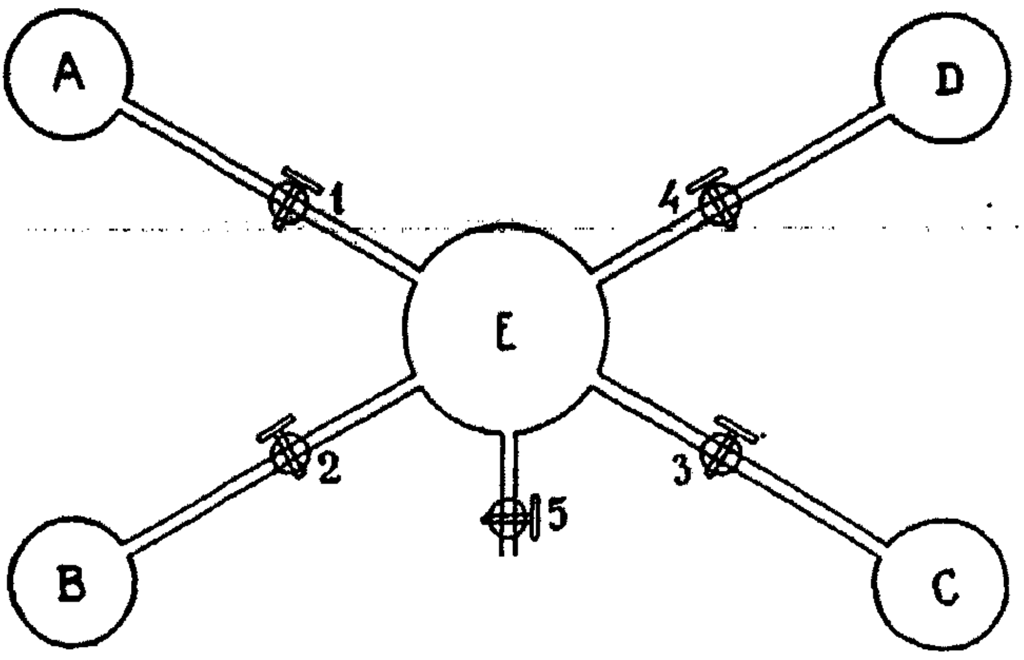

FIG. 2

DETERMINATION OF THE COMPOSITION CORRESPONDING TO THE EQUILIBRIUM STATE

In the previous work the composition of the liquid in a state of equilibrium was determined by considering the function:

$$t = f(K')$$

where t is the boiling point of the mixture at the pressure of 1 atmosphere and

$$K' = \frac{c_3'c_4'}{c_1'c_2'}$$

c_1', c_2', c_3', c_4' being the concentrations of the acid, alcohol, water, and ester respectively. On plotting the values of K' against t a curve is obtained which allows us to find the equilibrium constant $K = \frac{c_3c_4}{c_1c_2}$, when the boiling point, t_C, of the equilibrium mixture is known, or may be determined by extrapolation. In the present investigation the method of determining the constant K or the concentrations, c_1, c_2, c_3, c_4, corresponding to the equilibrium state, has been considerably improved and simplified. It consists in the following operations. When the equalization of the boiling points of the two mixtures is reached, a mixture M is prepared, which is very near to the equilibrium state, but still contains a small excess of water and ester. This mixture is introduced into the third ebullioscope C. Subsequently a corresponding mixture of acid and alcohol, N, is prepared and introduced into a bath at 0°C. Then the bulbs of the three ebullioscopes, A, B, and C, are heated and the boiling points t_A, t_B and t_C determined by means of the same thermometer. The liquids boil under some unknown pressure p'. Let the boiling temperatures be unequal, say $t_A > t_B > t'_C$. As mentioned above, the difference, $t_A - t_B$, is small and does not exceed 0.010°C. Now the stop-cock 3 is closed, the bulb of the apparatus C cooled and a small quantity of the liquid N, containing alcohol and acid, is introduced. The measurements are repeated by reading again the temperatures in A, B, and C. After repeating this procedure several times, a mixture is finally obtained which has a boiling temerature t_C fulfilling the condition: $t_A > t_C > t_B$. In order to obtain a complete series of data, it is necessary once more to add the same quantity of the mixture N containing acid and alcohol, and to find that the boiling point of the liquid in C is now higher than that of two others, say $t''_C > t_A > t_B$. With all these data the composition of the equilibrium mixture may be obtained without any difficulty.

When the boiling point of the mixture in equilibrium is known, a fourth ebullioscope, D, filled with water is used. After opening the stop-cocks 3 and 4 the boiling temperatures t_C and t_D are measured under the pressure existing in the system. Then a manometer filled with water is connected through the stop-cock 5 and a series of determinations of the boiling points of water (t_D) and of the liquid (t_C) at different pressures is carried out, in order to determine the value of $\frac{dt}{dp}$ for this liquid and obtain from it by calculation the boiling point at 760 mm. of mercury.

Up to the present, we have carried out several investigations only on the reaction that takes place in the formation of ethyl acetate. It is quite clear, however, that the same method may be applied in many other cases.

EXPERIMENTAL DATA

Three series of experiments were made in order to test the application of the method described. The reacting substances were carefully purified by methods described in previous papers and the mixtures weighed out by means of the apparatus previously described (4).

TABLE 1

EXPERIMENTAL VALUES	I	II	III
1. Proportion of alcohol and acid.....	1:1	3:1	1:3
2. Initial temperature difference Δt_0...	0.061°C.	0.233°C.	0.605°C.
3. Time in days......................	25	42	44
4. Final temperature difference, Δt...	0.000°C.	0.002°C.	0.008°C.
5. Number of drops, n..............	120	108	109
6. Correction for the dead space......	−0.018°C.	−0.014°C.	−0.048°C.
7. Correction for overheating.........	−0.033°C.	−0.034°C.	−0.034°C.
8. Boiling point corresponding to the equilibrium state................	76.25°C.	73.66°C.	90.78°C.
9. Equilibrium constant, K...........	3.82	2.47	4.74

TABLE 2

Changes in $t_A - t_B$ with time

3 moles alcohol and 1 mole acetic acid

TIME	CHANGES IN $t_A - t_D$	TIME	CHANGES IN $t_A - t_B$
days		*days*	
0	0.340	43	0.023
2	0.320	54	0.009
5	0.290	64	0.003
14	0.182	65	0.002
24	0.087	66	0.001

In table 1 the following data are given: (1) the proportion of ethyl alcohol and acetic acid in the "initial" mixture; (2) the initial temperature difference, Δt_0; (3) the time of duration of measurements, in days; (4) the final temperature difference, Δt, when the equilibrium state was taken as "established"; (5) the number of drops, n, flowing through the drop-counter per minute; (6) the correction for the dead space of the ebullioscope; (7) the correction for the overheating of the liquid; (8) the boiling point of the liquid in equilibrium at 1 atmosphere (compared with the boiling point of water as the standard substance); (9) the equilibrium constant K. The experiments were made by Sobolewski (column I), Kwiecinska (column II), and Bochenk (column III).

Table 2 illustrates the changes in the difference $t_A - t_B$ with time. It is a repetition of experiment II and was carried out by Dobry-Szapiro.

It seems that this difference, after several transports of the thermometer from one apparatus to the other, may be established with an accuracy of 0.001° – 0.002°C. It is very probable that this accuracy is greater than that in the determination of the boiling point of the reacting liquid in the pure state. The method thus allows of more accuracy than the method of preparation of the pure liquid substances, and the figures in table 4 should be considered to apply to the substances used in our experiments. In two experiments where different samples of reacting substances were used, the mixture when in the equilibrium state gave a difference between the boiling points equal to 0.017°C., whereas the differences $t_A - t_B$ observed for the two mixtures in one experiment did not exceed 0.002°C. Table 3 gives an example of the method for determining the composition of the equilibrium mixture, C, and its boiling point.

TABLE 3

ALCOHOL	ACID	ESTER	WATER	$K = \frac{c_3c_4}{c_1c_2}$	Δt
					degrees C.
0.9242	0.0404	0.4018	0.4018	4.321	0.202
0.9233	0.0389	0.4033	0.4033	4.529	0.091
0.9225	0.0381	0.4041	0.4041	4.646	0.027
0.9221	0.0377	0.4045	0.4045	4.707	0.010
0.9218	0.0374	0.4048	0.4048	4.753	0.003

TABLE 4

Values of K obtained by Swietoslawski and by others

$\frac{\text{MOLE ALCOHOL}}{\text{MOLE ACID}}$	K			
	Ebullioscopic method	Poznanski	Blaszkowska	Tobbin
1:1	3.82	3.79	3.76	3.70
3:1	2.47	2.45	—	—
1:3	4.74	4.72	—	—

The calculation of K can be performed with great accuracy. In table 4 we have given for K only two decimals because we consider that the methods of purification of the reacting substances are not sufficiently trustworthy to guarantee the third decimal. In table 4 is given a comparison of the data obtained by us and by other authors (5).

SUMMARY

The ebullioscopic method for determining the composition of equilibrium mixtures seems to be very accurate and is applicable in all cases where the boiling temperature of the equilibrium solution differs considerably from the boiling points of the initial mixtures of reacting substances. The preparation of the equilibrium mixtures, when the equilibrium has been established, may be performed with a high degree of accuracy. In the case of the formation of ethyl acetate the ebullioscopic method is even more trustworthy than the methods of purification of the reacting substances. The values for the equilibrium constant of esterification in the liquid phase have been found for mixtures whose initial composition was 1 mole ethyl alcohol: 1 mole acid, 3 moles alcohol: 1 mole acid, and 1 mole alcohol: 3 moles acid. The boiling points of the corresponding equilibrium mixtures were found to be: 76.25°C., 73.66°C., and 90.78°C., respectively.

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PHOTOVOLTAIC EFFECTS IN GRIGNARD SOLUTIONS. III

New Observations. A Possible Theory

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This article[1] records certain new observations on photovoltaic effects in Grignard solutions and in other substances, and outlines briefly certain theoretical considerations which may apply to the effect. The work is a continuation of that described in previous papers by the writer (1).

NEW OBSERVATIONS

The results here reported are summarized from observations on about eighty cells, some of which, because of changes of electrodes or other experimental conditions, are equivalent to several single cells each. About sixty of the cells contained Grignard solutions, and about twenty were cells of other types which it was desired to study for purposes of comparison. In all, results are now available from more than three hundred cells, on which the total number of readings would probably exceed two hundred thousand.

The tests with the device for circulating the solutions, described in the previous paper (1), have been continued; so far, they seem to confirm the conclusions stated there. The writer wishes to make further experiments before stating final conclusions; the question whether two effects exist is still open, though the conclusion seems very probable.

For work in this field, it would be very convenient if some electrode could be found which would be entirely free from any response to light, when immersed in Grignard solutions. So far, no substance has been found which does not give some small photovoltaic effect in these solutions. Mercury covered with carefully dried calomel, in ethylmagnesium bromide solution, gives only a few millivolts; probably the calomel protects the mercury surface from the light, or from the products formed by the light. But even this small response is thirty to forty times the error of measurement. And with phenylmagnesium bromide, the solution becomes discolored. Hence this type of electrode, while perhaps the most nearly inactive so far found, is

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[1] Abstracted from a thesis presented to the Graduate School of the University of Missouri in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1931.

far from satisfactory. It is therefore necessary in studying the responses of single electrodes to use H-shaped cells in which the electrode in one arm can be kept completely dark. While these cells give satisfactory results, they require the use of larger volumes of solution than would otherwise be necessary. The use of standard reference electrodes, such as the calomel half-cell, has not been attempted, because of the diffiulty in bridging over from aqueous solutions to ether solutions which must remain absolutely anhydrous, and because of the uncertainty concerning the electromotive forces that might be introduced at the liquid junctions. A really inactive electrode would be very convenient.

The failure of phenylmagnesium bromide solutions to transport any considerable amount of effect of illumination with it in the circulation experiments seems to indicate that the effect in this case may be due to some kind of sensitive film formed on the electrode surface. The capacitance measurements made by Hammond (2) seem to make it clear that thin films always exist on the electrode surfaces in these cells. Tests reported in the preceding article (1) indicated that the response with platinum electrodes in Grignard solutions is not due to adsorbed oxygen; electrodes held at 800°C. in a hydrogen atmosphere for some hours, and cooled in hydrogen, behaved the same as electrodes flamed and cooled in air, or electrodes kept between slices of sodium in ether. These precautions seem sufficient to exclude the possibility of effects due to oxygen, which might have been expected to produce some effect if present in or on the electrodes, where it could react under the stimulation of light. Electrodes cooled in nitrogen behave similarly. It seems probable, therefore, that the regularly observed effects are not due to films of gas on the electrodes.

However, it seems very clear that other kinds of film on the surface of a platinum electrode can affect its response to light. For example, a film of the oxidation product formed by the momentary exposure of an electrode wet with Grignard solution to the air, or the film formed by dipping a moist electrode into a Grignard solution, will change the behavior of a platinum electrode, as shown in figure 1. These films raise the dark voltage to unusually high values, sometimes more than one volt, and they increase the resistance of the cells enormously. As the figure shows, the response to light may be even greater than without the film. Exact values of the thickness of these films cannot be given, but the order of magnitude is about 0.1 to 0.01 mm.

Preliminary results on several other metals in Grignard solutions are available. With lead electrodes, the presence of a surface layer of oxide seems to make no important difference in the response. With aluminum, the response is slightly larger if the layer of oxide is left on the surface, as the sheet comes from stock, than if the sheet is freshly polished just before inserting it in the solution. Clean copper surfaces show a good response.

Surface layers of oxide give rise to differences in the response which are undoubtedly due to the light-sensitiveness of the cuprous oxide itself. The response of cuprous oxide in the solutions mentioned is less than in some aqueous solutions that have been studied.

The curve in figure 2 was obtained from a type of cell obtainable commercially, which contains a sensitive electrode of cuprous oxide on copper, an inert electrode of lead, and a solution of lead acetate or nitrate. The curve was obtained with potentiometric equipment, so that the cell supplied no current except the minute amounts used in obtaining balance. Used with a milliammeter, the response and recovery of the cell are even more rapid—too rapid for an instrument to follow. The current changes from zero in the dark to several milliamperes in intense light. The tendency to reach a

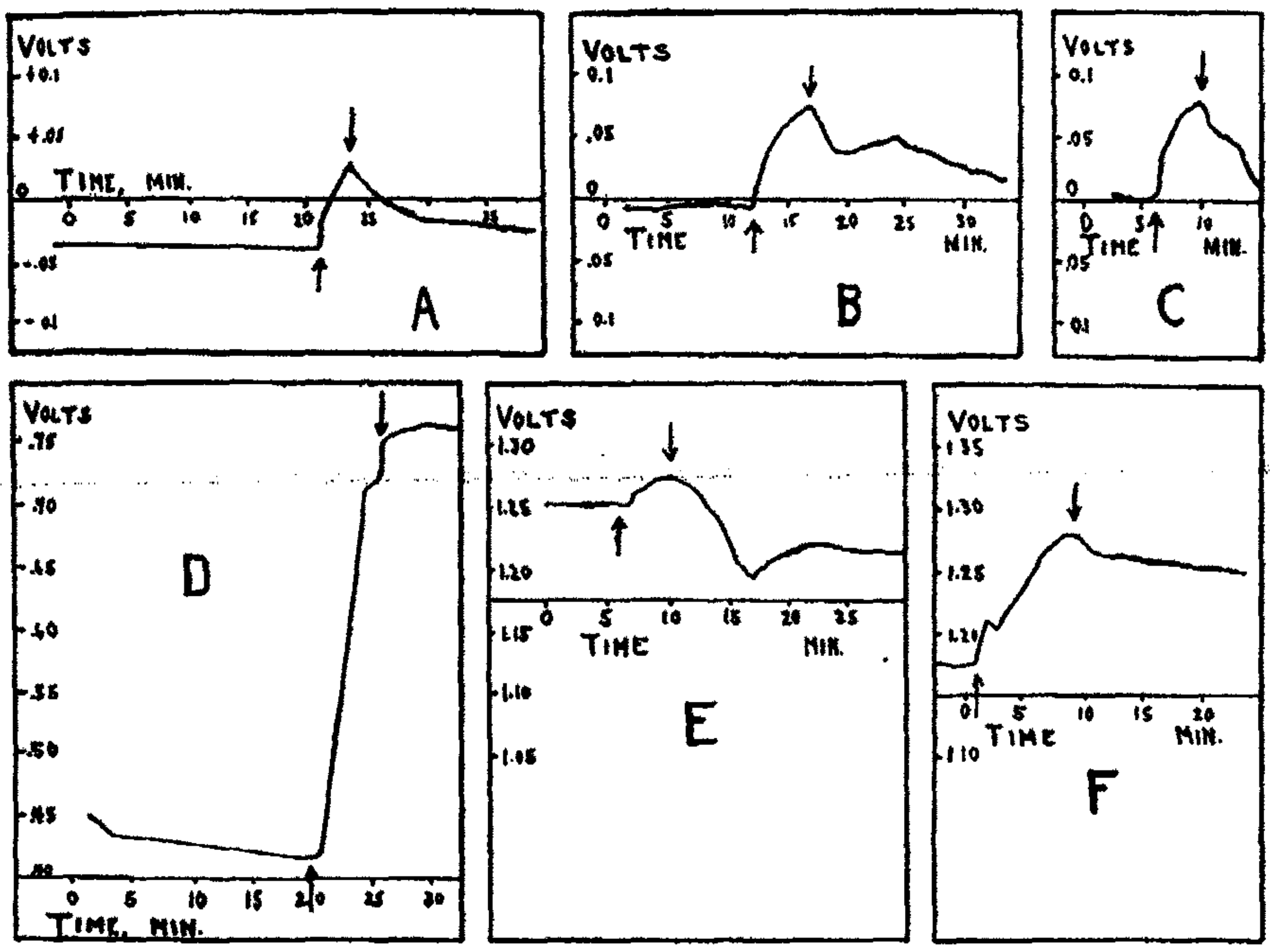

FIG. 1. CELL NO. 101, Pt | C_6H_5MgBr | Pt, WITH ONE PLATINUM ELECTRODE ILLUMINATED

Curve A is for a clean bright platinum electrode; curves B and C are for another similar electrode, but taken on different days. Curve D is for the electrode of curve A after it was coated with the oxidation products from the Grignard reagent; curves E and F are for other coated electrodes coated with hydrolysis products of the Grignard reagents.

The upward-pointing arrows indicate the time at which illumination begins; the downward-pointing arrows indicate the end of the illumination.

maximum response quickly, and then to show a decreasing response with continued illumination, seems to be usual in cuprous oxide.

Cells with sodium and potassium electrodes in Grignard solutions have been given some study. The metals were cut and handled under anhydrous ether, except that they were kept in a nitrogen atmosphere while they were transferred to the solutions. The surfaces, bright when first cut, become bluish gray on standing. This change of color probably indicates formation of some kind of surface film on the electrodes; but it is doubtful if the films contain oxygen, or if they do, whether these metals would release

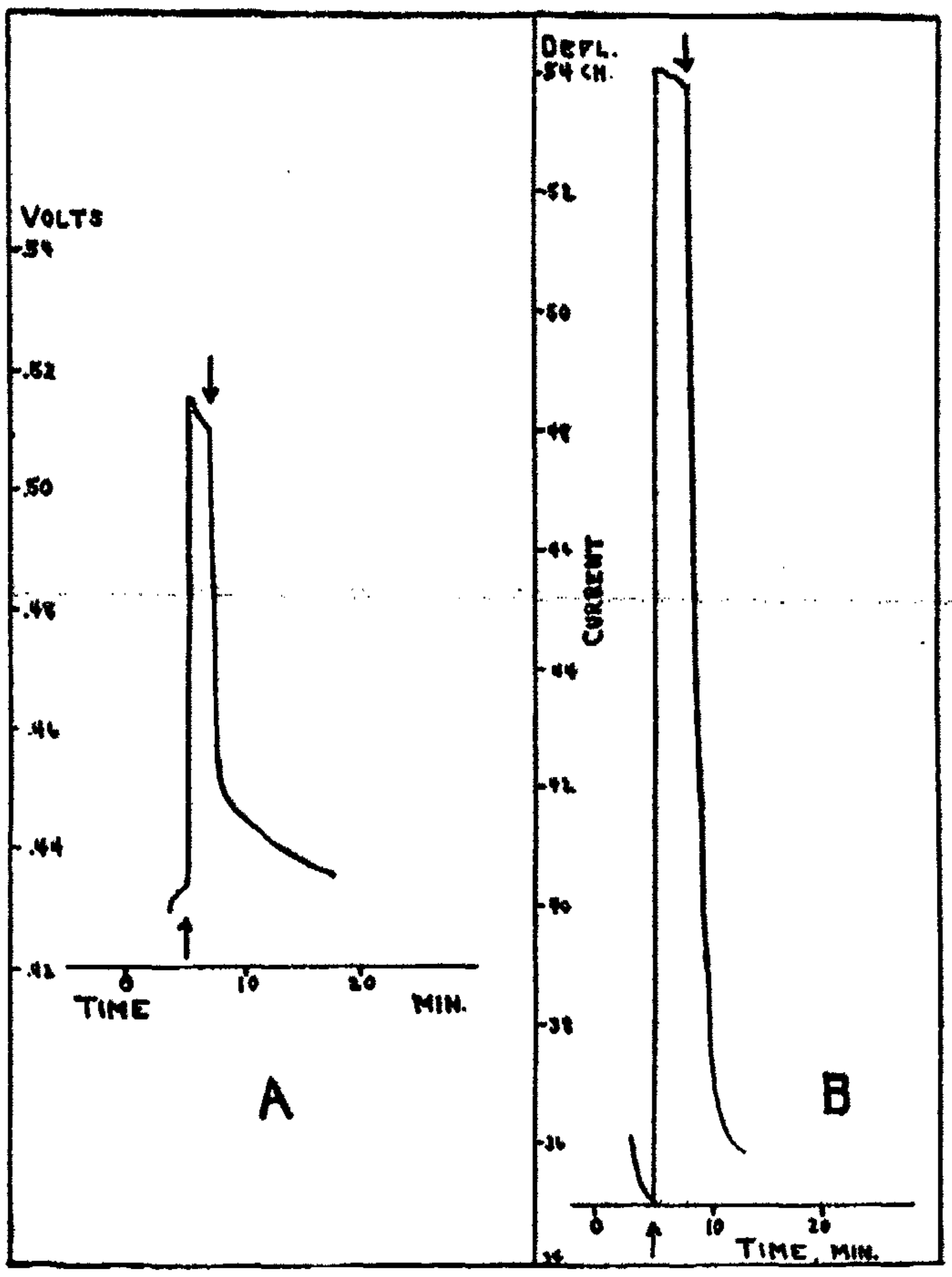

FIG. 2. CELL NO. 401, A COMMERCIAL TYPE OF PHOTOVOLTAIC CELL, Cu | Cu_2O | $PbC_2H_3O_2$ | Pb

Curve A shows the voltage response, curve B the current-response, to white light. This type of cell gives larger responses than the types referred to in figure 5.

it under illumination. The sodium electrodes gave small but remarkably consistent responses both to light and to x-rays. Typical curves are shown in figure 3. The potassium gave smaller and more erratic responses; on standing a few days, the metal dissolved completely, and was replaced by a dark fibrous mass, probably magnesium deposited electrolytically by local action. This reaction deserves further study.

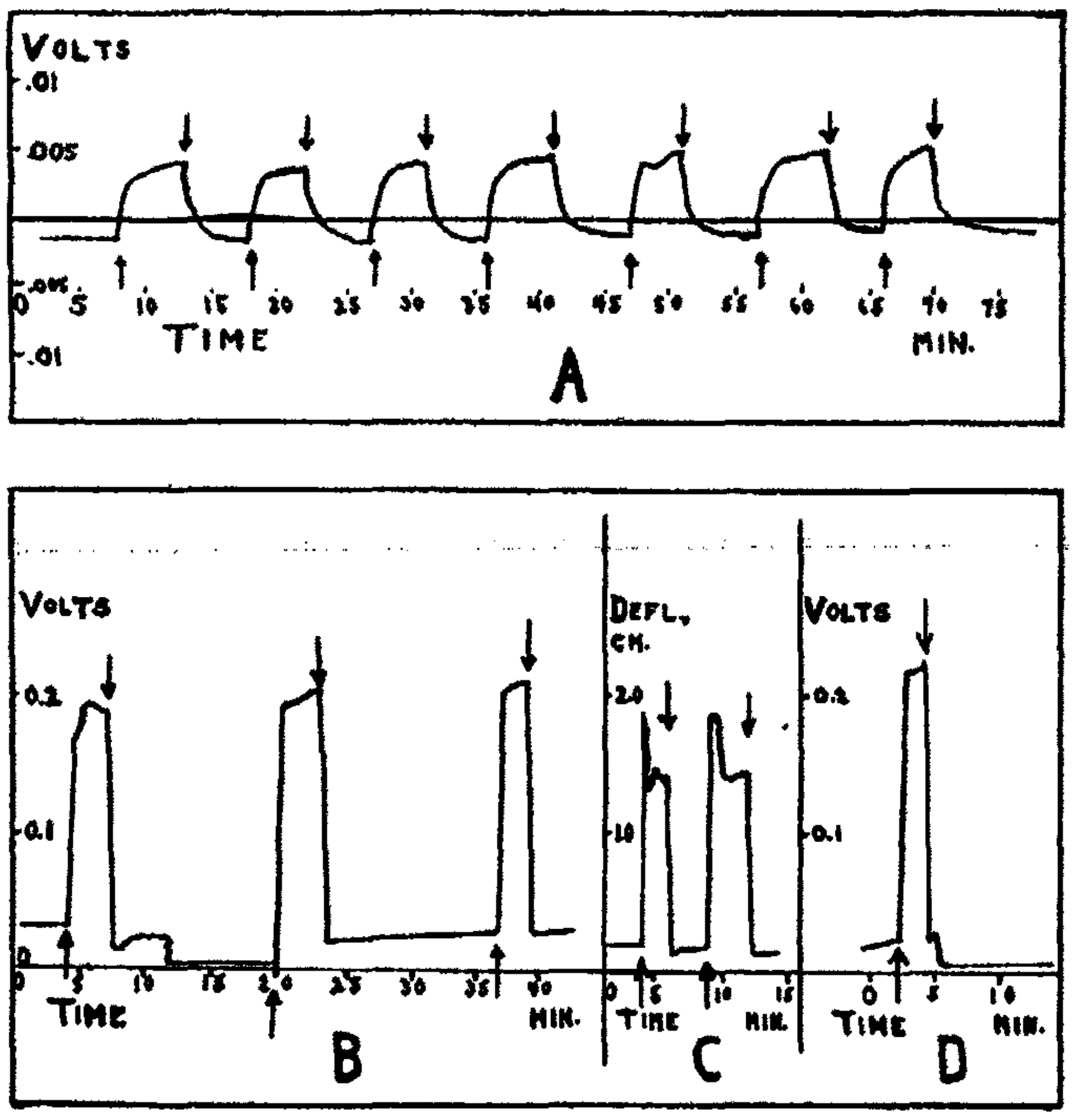

FIG. 3. CELL NO. 105, Na | C_2H_5MgBr | Na, ONE ELECTRODE ILLUMINATED

Curve A shows the response to white light, the results being unusually reproducible. Curve B shows the voltage response of this cell to x-rays; curve C the current-response to x-rays; and curve D shows another voltage response curve taken just after the current curves were obtained, showing that polarization by the current did not affect the reproducibility of the voltage responses.

Somewhat similar cases of formation of sensitive films in aqueous solutions are known. Grube and Baumeister (3) and others have studied the light-sensitivity of anodically polarized platinum electrodes. The response is of the type that shows a reversal on continued illumination. On the other hand, the writer found that anodically polarized aluminum in aqueous solutions is relatively insensitive both to visible light and to x-rays. Ultraviolet light gives a small but consistent effect.

The general conclusion from these observations seems to be that while surface layers do not necessarily cause photovoltaic effects to appear, they do modify the effect frequently, and may in some cases be responsible for the appearance of the effect. The experiments described above seem to indicate that the effect is not due to oxygen in all cases. The study of such surface effects seems to the writer to be well worth continuing, since it seems probable that the results can be of great help in deciding the nature of photovoltaic action. The study of the effects of depolarizers, described briefly in the preceding article, seems equally promising, and is being continued.

A number of cells have been made in which Grignard solutions were hermetically sealed in glass. These cells have shown a good response to light after three years; under proper conditions, therefore, their useful life is considerable.

In collaboration with Dr. H. E. Hammond, the writer has studied the response of a number of Grignard cells to x-rays. In general, the responses obtained have been large compared with those from visible light; a typical case is shown in figure 4. They seem to obey the same logarithmic law as applies to other cases of the photovoltaic effect, though the law is only a very rough approximation. These observations were made under conditions in which the shielding of the circuits was not entirely satisfactory, so that there is some possibility that electromagnetic induction, together with rectifying properties of the cells, could give rise to a spurious effect. While auxiliary experiments made at the time seemed to prove that such spurious effects were negligible, there were discrepancies in the behavior of certain cells which did not seem explainable otherwise. The results are therefore regarded as preliminary, and are communicated with due reservation. More satisfactory apparatus has been prepared, and additional work is to be carried out with it. The effect gives some promise as a method of measuring x-ray intensities.

It is interesting to compare with the preceding results the curves obtained from photovoltaic cells which contain no electrolyte. The light-sensitive substance was either cuprous oxide or selenium, though other substances are known which give the effect. Such cells can be made by forming a layer of cuprous oxide on copper by heating (such plates are used commercially in the cuprous oxide type of rectifiers which have come on the market recently), and then pressing a layer of wire cloth against the oxide, or plating or sputtering a metal layer on it. When illuminated through the wire cloth, current tends to flow, the wire cloth becoming positive by several hundredths of a volt. While some investigators have regarded this phenomenon as a photoelectric effect, the writer has included it with the photovoltaic effects, since it is essentially the production of an electromotive force by light, and since the response not only follows the same roughly logarithmic law as other photovoltaic effects, but shows the same tendency to diminish and even to reverse its direction under prolonged intense illumination. Typical curves are shown in figure 5. Copper and nickel wire cloths have been used, the nickel giving a somewhat larger response. The response and recovery are very rapid in these cells, so that they can follow fluctuations in the illumination up to frequencies of 1000 per second, beyond which the response becomes small. Their dark voltage is usually zero. The reversal of the response is shown in the last two illuminations in figure 5. The recovery from such a reversed response is direct; positive values are not retraced. Subsequent responses are reversed. It is not known how long such a negative response would continue; the cell which gave the curve reproduced here had completely recovered its normal charac-

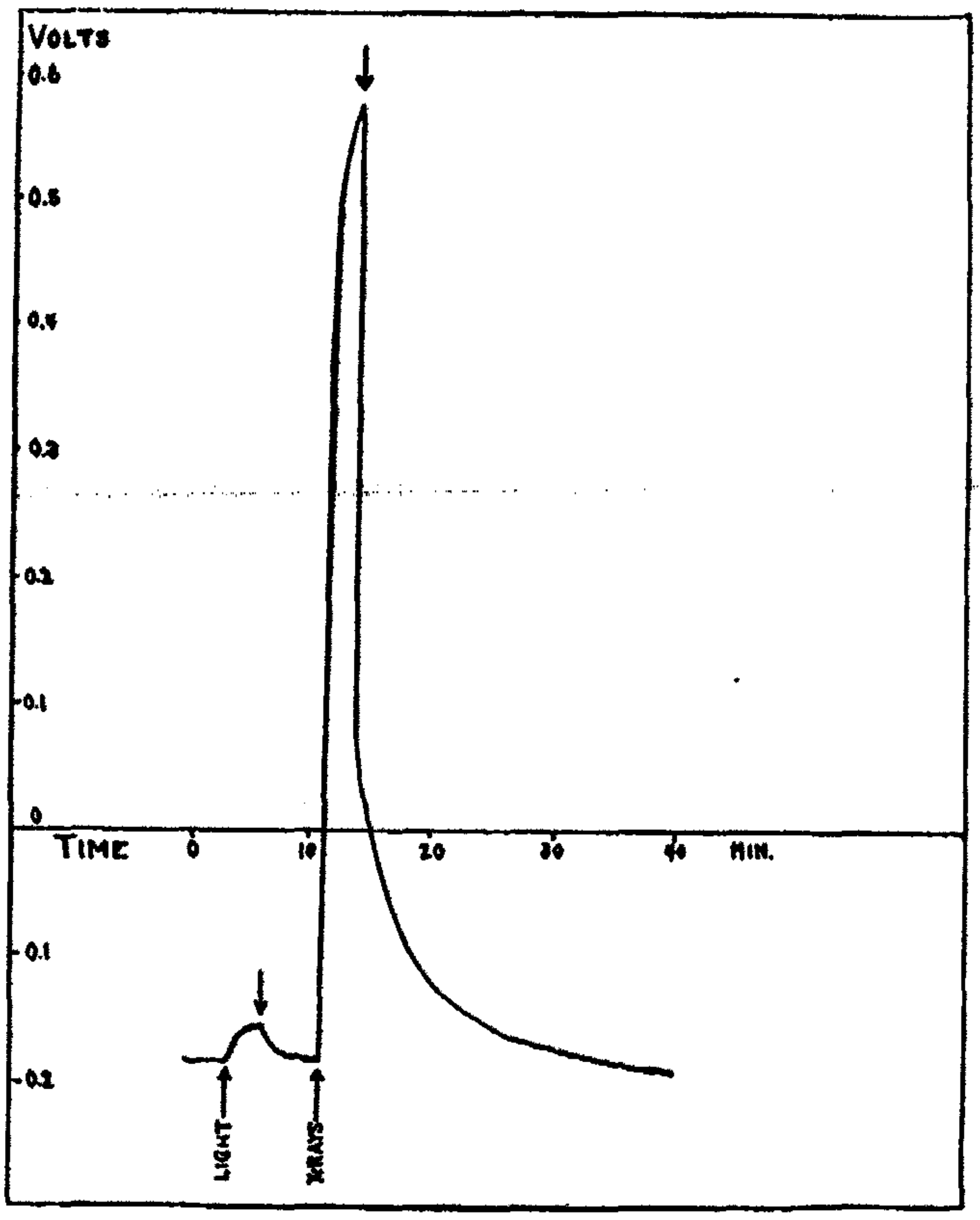

Fig. 4. Cell No. 107, Pt | C_6H_5MgBr | Pb, Platinum Electrode Illuminated

The curve compares the voltage response to intense white light with that obtained from x-rays. The latter effect is being reinvestigated.

teristics by the following morning. The reversal seems to occur equally quickly whether the cell delivers maximum current or none. Substances which behave in this respect like cuprous oxide, generally show a reduction in electrical resistance on illumination. They also show a certain amount

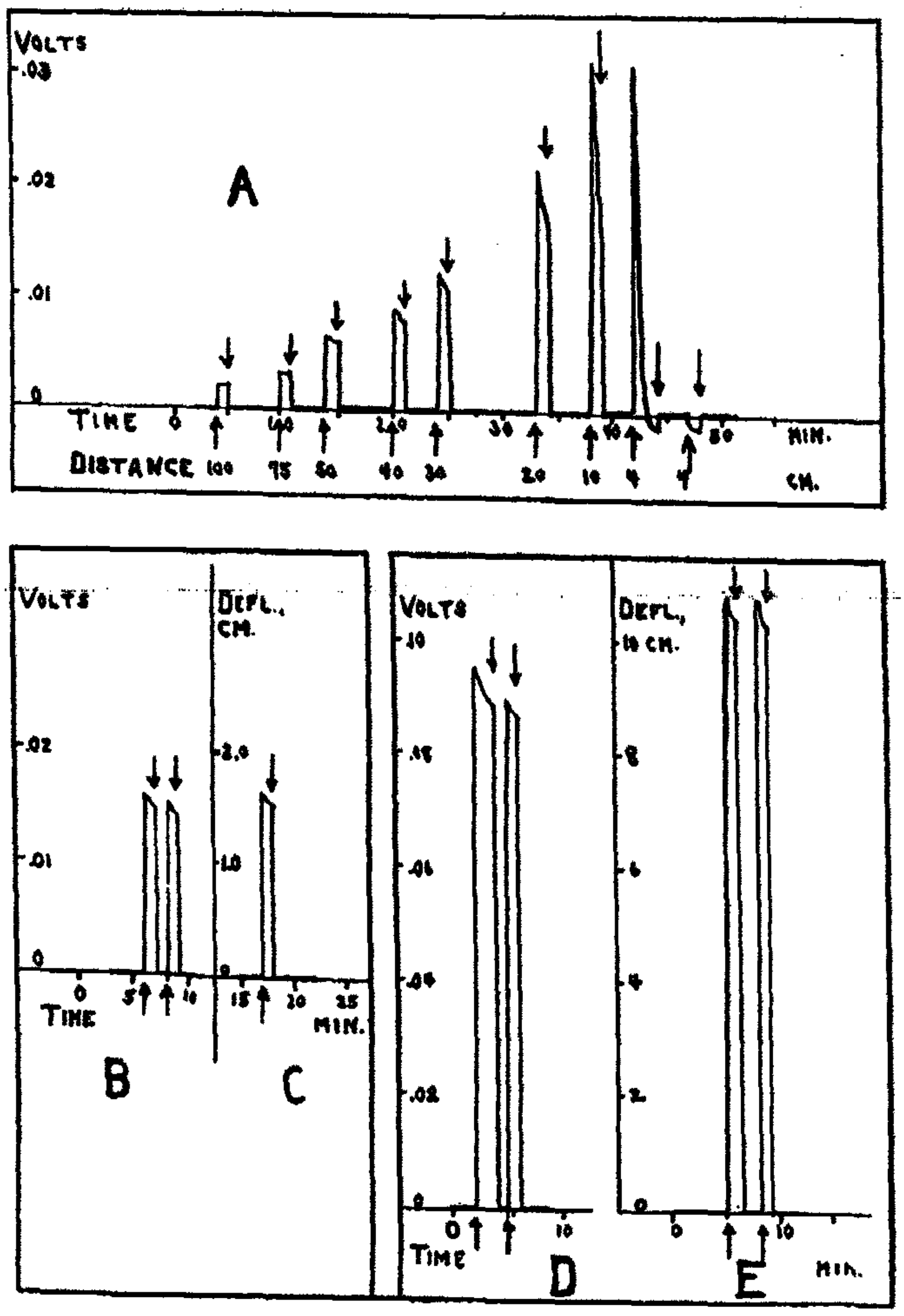

Fig. 5

Curve A shows the voltage response to white light of different intensities, of Cell No. 400, Cu | Cu_2O | Cu, a "dry" cell with the outer coating of copper electroplated on the Cu_2O. The reversal of the voltage response on intense illumination is noteworthy. Curves B and C compare the voltage and current responses of Cell No. 405, a dry Cu | Cu_2O | Cu cell in which the outer electrode was a copper wire cloth pressed against the cuprous oxide, with the similar responses in curves D and E for Cell No. 404, a Ni | Cu_2O | Cu cell with the copper wire cloth replaced by one of nickel.

of unilateral conductivity, which permits their use in rectifiers. Some writers have claimed that the rectifying ability and the photovoltaic responses are directly proportional to each other, but this statement is disputed by others.

The striking similarity of the behavior of these dry cells to that of electrolytic cells raises the question whether the effect in the dry cells can be due to traces of moisture. Apparently the answer to this question is negative. One such cell was kept heated to above 100°C. for some time, then was cooled in a desiccator in which it was kept for several weeks. Its characteristics were not changed at all.

THEORETICAL CONSIDERATIONS

It seems worth while now to examine the experimental evidence so far obtained, in search of indications as to the probable nature of the processes that underlie the photovoltaic effect. In discussing photovoltaic effects, it is usual to divide the phenomena into two classes: (a) the group in which the electrode is the light-sensitive part of the cell (this is the type discovered by Becquerel); and (b) the type in which the electrolyte is the sensitive part. But the Grignard cells containing solutions of substances like phenylmagnesium bromide, which transport little or no effect with the electrolyte but instead seem to form a sensitive layer on the surface of an otherwise inert electrode, seem to belong in a third class, or at least in a very special subdivision of the second. The dry cells containing substances like cuprous oxide or selenium, but no electrolyte, seem to belong in a still different class, which quite possibly should include some of the cases usually placed in the first group. While many authorities regard the last group as photoelectric rather than photovoltaic in nature, they are placed in the latter class here because of the very great resemblance of their behavior to that of other kinds of photovoltaic cell. The points of resemblance may be stated, for emphasis: (a) the effect observed is a change in electromotive force; relatively large currents can be obtained, but the currents are not always proportional to the illumination; (b) the responses occur with wavelengths too long to excite a surface photoelectric effect in the substances concerned, so that it must be explained by a special internal photoelectric effect if it is due to such an effect; (c) the maximum electromotive force developed is roughly proportional to the logarithm of the illumination, and not a linear function of it, nor is it a linear function of the frequency; (d) the maximum current obtainable is likewise not always proportional to the illumination, at least for high intensities of illumination, but is more nearly proportional to the logarithm of the illumination; (e) the E.M.F. decreases and sometimes actually reverses on long-continued illumination; (f) the response shows a time lag so great that such cells cannot follow light variations of frequency very far above 1000 per second. It is of course true that dry cells show differences in behavior from that of the other classes: they respond and recover more rapidly; the response and recovery curves are somewhat different in shape, possibly indicating a different mechanism for the response; and they show relatively large decreases in resistance when illuminated.

The statements which follow are intended to apply primarily to the effects observed in Grignard solutions, although they apply to a certain extent in a great many other cases. It is not yet possible to give an entirely satisfactory theory of all photovoltaic effects. The writer regrets sincerely that the severe limitations of available space at present necessary have compelled omission of adequate review or reference to the many theories presented by other workers. A picture is here suggested tentatively as being a probable one; it necessarily contains many elements suggested by other workers, but contains a few points that are apparently new.

There are strong reasons for doubting that the effect can be due simply to the emission of electrons under the influence of light. One such reason is the existence of "Minchin reversals," in which the photovoltaic E. M. F. reverses its direction if the illumination is continued. This may not be a conclusive argument, since it has been shown earlier in this article that the same type of reversal can be obtained from the "dry" type of photovoltaic cell, in which the effect is usually explained as being due to the emission of photoelectrons at a barrier layer. However, it may be that this commonly accepted explanation of the action in dry cells is incorrect. Another reason for doubting the simple electronic explanation, in the present case, is the fact that some of the solutions carry the effect with them, when circulated, so that a previously illuminated solution can affect an electrode in the dark, just as if the electrode itself had been illuminated. Not all of the solutions seem to be able to do this; but the fact that some of them do suggests that the effect depends in some way on the formation of either ions or excited molecules by the light. Other reasons for doubting the electronic theory are suggested in the second paragraph above; the theory is quantitatively unsatisfactory in several respects.

The suggestion that light actually ionizes the solutions seems to be definitely contradicted by the experimental evidence. If a Grignard cell be regarded as a concentration cell, for the purpose of computing the change in the concentration of the ions controlling the electrode potential that would be necessary to explain the observed changes in E. M. F., it is found that the concentrations would need to change in a ratio which often would exceed a millionfold. From the conductivity, the ionization is already considerable, and any such change as demanded by the theory would almost certainly give rise to a measurable change in the conductivity of the solutions. This point has been tested thoroughly. Hammond (2), in a number of measurements of the resistance of such cells, found that the changes produced by light were very small. In one case a 2 per cent change was observed, but all the others were considerably smaller. Harty (4), in a large number of measurements, found that the changes rarely exceeded one-half of 1 per cent. In the majority of observations, the change was an increase rather than a decrease in resistance, as if the light had suppressed rather than increased the ionization. In view of these facts, it seems more probable that light produces some type of excited molecules, rather than ions.

It is very likely that the electrodes in the Grignard solutions are covered by layers of adsorbed molecules, which probably are not in quite the same state as the molecules in the solution. There are two chief reasons for such a statement. First, the direct-current resistance of the cells often exceeds the electrolyte resistance, as determined by alternating-current methods, by as much as a thousandfold. Apparently the D. C. resistance is due largely to polarization. It can be decreased by the addition of suitable depolarizing substances. Further, the capacitance of these cells, which can be determined simultaneously with the A. C. resistance, proves to be very large, so that the most reasonable interpretation of the observations seems to be that the capacitance is that between electrodes and electrolyte. Since values of as high as seven microfarads per square centimeter have been observed, it appears that the relatively non-conducting film that covers the electrodes is often only a few molecules thick, possibly at times only one. The sensitiveness of the voltage of some of these cells to shaking may indicate that in some cases these surface layers are very loosely held. The variability of the dark voltage suggests that the films may be continually changing. The photovoltaic effect is then visualized as being due to the formation of excited molecules by the light, either throughout the liquid or, in some cases, only in the layer of electrostatically strained molecules making up the surface film on the electrode; the surface-layer molecules are then more or less completely replaced by excited molecules which are formed in the layer or which drift in to it, or else the excited molecules form an additional layer on the electrode surface. There is evidence in the capacitance measurements of Hammond and of Harty that both of these possibilities actually occur. These adsorbed layers of molecules introduce adsorption potentials which must modify the potentials of the cells.

The action of depolarizers in reducing the D. C. resistance of the cells seems to be due to the substitution in the surface films on the electrodes of other molecules which offer less hindrance to the processes which occur at the electrode surfaces in conduction. The depolarizing substances are not good conductors by themselves, and it is found that at the same time that they reduce the D. C. resistance of the cells, they increase the electrolyte resistance, as would be expected from diluting the electrolyte with a nonconducting liquid. The depolarizing action occurs in systems in which there seems to be no possibility of chemical reaction, and no other explanation than the one just suggested has been put forward for such cases.

While the subject is by no means settled, it is probable that no photochemical reaction occurs in the Grignard solutions which is able to explain the observed photovoltaic effects. It is the opinion of the writer, based on a considerable amount of evidence collected from the literature as well as from observation, that even in those cases in which photochemical reactions are known to occur, in most cases a photovoltaic effect exists independently of and in addition to the changes in E. M. F. due to the chemical reaction.

In view of the facts, now well established (new evidence on this point will be forthcoming from the writer's laboratory later), that a photovoltaic effect can exist independently of fluorescence of or any selective absorption of light by the electrolyte, it seems certain that any idea of a necessary association of these phenomena must be abandoned.

A suggestion as to the nature of the excited molecules postulated above may add a clarifying detail to the picture presented. Most writers have suggested simply an electronic displacement for the excitation process. However, such excitation is usually associated with selective absorption, and, judging from the duration of the associated fluorescence, the life of excited molecules of this type is entirely too short to explain the long-continued photovoltaic effects. It seems that for the present purpose something further is needed. Either more stable types of electronic displacement than are known from other phenomena must be assumed, or else other types of excitation must be sought. Now, another type of excitation is known, from its occurrence in connection with the Raman effect. In this type, the atoms which make up the molecules are separated somewhat by the light, and are set in vibration, the frequency of the internal vibrations being related to the characteristic infra-red frequencies of the molecules. Whether excitation of this type is sufficiently long-lived to explain photovoltaic effects is not known. The writer believes that either this type, or a similar type in which the vibration is missing and the life is longer, will be found able to supply the necessary mechanism for explaining photovoltaic effects. For a given molecule, there are as many types of excitation of this sort as there are types of interatomic linkages. It seems necessary, and not unreasonable, to suppose that at least two types of excited molecules are formed in the cases in which reversals occur; if the type which forms more slowly, or which diffuses to the electrodes more slowly, is also the more stable type, so that its effect ultimately outweighs that of the less stable variety, a possible basis is found for at least a qualitative explanation of the reversal phenomena.

The picture suggested has been described very sketchily and with many details omitted, since it is still in the formative stage. It has, however, already justified itself from the point of view that it has suggested many new experiments which have yielded valuable information regarding the photovoltaic effect.

The writer is grateful to Professors O. M. Stewart and H. M. Reese, of the Department of Physics, the University of Missouri, for continued encouragement and support of this work; and to the gradually increasing group of graduate students who by working out important details are making possible more rapid progress on the problem. Thanks are due the Research Laboratory, Incandescent Lamp Dept., General Electric Co., Cleveland, Ohio, and to Mr. Samuel Wein, of New York, for certain materials used in this work.

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STUDIES IN COPRECIPITATION. VI

INTERNAL STRUCTURAL CHANGES ON AGING OF FRESHLY PREPARED PRECIPITATES

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Studies made in recent years show that the lattice of a real crystal is far from ideal. Crystals seem to be built of submicroscopic or amicroscopic blocks, the so-called Smekal (1) blocks, which fit together like bricks in a wall, giving rise to free spaces in the packing (Lockerstellen). In addition, ordinary crystals very often even contain microscopically visible cavities. A real crystal therefore has a very discontinuous structure and possesses a large internal surface. D. Balarew (2) has strongly advocated the theory that contaminating substances are adsorbed at the internal surface of a crystal, and goes so far as to attribute all coprecipitations to this cause.

In previous studies dealing with the corprecipitation of water and of foreign ions with calcium oxalate, it was found that contaminants appeared to diffuse out of the crystalline precipitates if the latter were allowed to age under the mother liquor before filtration. This phenomenon cannot always be attributed to a recrystallization, for the particle size is often too large for this to occur to any extent. Therefore, under these conditions, it may be assumed that the contaminant actually diffuses out through microscopically invisible cracks and capillaries in the crystals. In other words, the fresh crystals are very imperfect immediately after precipitation, but on standing there is a tendency for the cracks and capillaries to become filled with lattice material, this process resulting in the pushing out of foreign substances. If the perfection of the crystals would take place in such a way that the capillaries were entirely filled with lattice ions, it might be expected that all the foreign material would be extruded. From the experimental evidence presented in this paper it would appear that the perfection does not take place in such an idealized manner; in most cases dams are formed in the capillaries, and these prevent further effusion of adsorbed material from the inside to the outside of the crystals. Such crystals may have a large "isolated interior surface," which no longer is in open communication with the outside. Moreover, a large part of the internal surface becomes isolated during the growth of the crystalline precipitate.

In the first part of this paper experiments will be described in which potassium iodate was added to a freshly formed suspension of calcium oxalate after the precipitation had taken place. After various times of shaking, the iodate in the supernatant liquid was removed by addition of iodide and dilute acid (insufficient to dissolve the precipitate but strong enough to allow a quantitative reduction of the iodate) and then thiosulfate; after the last trace of iodine had reacted, strong hydrochloric acid was added to dissolve the calcium oxalate, and the iodine liberated from the iodate in the precipitate quantitatively determined with dilute thiosulfate solution. In addition, experiments were made in which the effusion of iodate coprecipitated with calcium oxalate was investigated after various treatments. The experimental procedure in the determination of the iodate content of the precipitate was similar to that described above.

I. EXPERIMENTS WITH CALCIUM OXALATE

A. Decrease of amount of coprecipitated iodate in calcium oxalate on standing

Twenty-four cubic centimeters of 0.25 *N* calcium chloride mixed with 10 cc. of 0.050 *M* potassium iodate was treated at room temperature with 20 cc. of 0.25 *N* ammonium oxalate. The precipitate was allowed to stand in the liquid for the period of time indicated in table 1; 40 cc. of 0.10*N* hydrochloric acid and potassium iodide was then added to the mixture. The iodine thus liberated was titrated first with 0.1 *N* thiosulfate and then carefully with 0.005 *N* until all the iodine was just removed (starch as indicator). Concentrated hydrochloric acid was next added to dissolve all the precipitate and to liberate the iodate held internally. The amount of thiosulfate required to titrate the iodine liberated by the internal iodate is given in table 1.

The precipitate obtained under the conditions just described recrystallizes and grows to larger size on standing, as microscopic observations show, so that the decrease in contamination is not due primarily to effusion of impurity from the crystals. These results are recorded for the purpose of comparison with the next series of experiments, which were made under conditions such that there could have been but little recrystallization. The precipitates described in table 2 were obtained by Hahn's procedure at room temperature in the presence of 10 cc. of 0.050 *M* potassium iodate. The time of precipitation was 5 minutes. Twenty cubic centimeters of 0.25 *N* ammonium oxalate and 21 cc. of 0.25 *N* calcium chloride were used, the latter being kept 1 cc. in excess during the addition. The volume at the end of the precipitation was 100 cc.

It is evident that more than 50 per cent of the iodate has escaped from

Hahn's precipitate after twenty-four hours standing. It is improbable that this purification can be attributed to recrystallization, for the crystal size of the precipitate is larger than that of one formed by the ordinary method in the cold and which has stood for a week in solution. It should

TABLE 1

Dependence of amount of iodate in calcium oxalate precipitated cold on time of standing after precipitation

TIME OF STANDING	IODATE IN PRECIPITATE (AS CC. OF 0.005 *N* THIOSULFATE)	TIME OF STANDING	IODATE IN PRECIPITATE (AS CC. OF 0.005 *N* THIOSULFATE)
hours		*hours*	
0	14.2	4	10.3
0	13.0	19	8.4
$\frac{1}{12}$	11.8	19	8.65
$\frac{1}{12}$	11.9	70	8.7
$\frac{1}{12}$	11.6	73	8.5
$\frac{1}{12}$	11.5	120	7.8
2	10.5	48*	2.7
4	10.95		

* Liquid diluted to 225 cc. after precipitation. The high dilution decreases iodate concentration in solution and promotes recrystallization.

TABLE 2

Decrease of iodate content in precipitates (prepared according to F. L. Hahn) on standing

NO.	PROCEDURE	CC. OF 0.0050 N THIOSULFATE REQUIRED
1	Precipitate dissolved immediately after precipitation	42.9
2	Precipitate allowed to stand in solution from which precipitated, after 40 cc. of 0.10 *N* hydrochloric acid had been added and iodine removed, for 18 hours. Precipitate then dissolved and titrated with thiosulfate after removing free iodine. When titrated required..........................	24.6
3	Precipitate washed to remove iodate and allowed to stand in 100 cc. of solution containing 4 cc. of 0.25 *N* calcium chloride for 25 hours	Supernatant liquid contained iodate equivalent to 19 cc. of thiosulfate and the precipitate 23.8 cc.
4	As in 3; stood 48 hours	Supernatant liquid then required 21.1 cc. of thiosulfate and the precipitate required 18.5 cc.

also be remembered that Hahn's precipitate formed at room temperature contains very little higher hydrate, so that the purification cannot be ascribed to the transformation of the higher hydrates into the monohydrate.

Precipitates formed in hot solution generally show only a slight loss of iodate or other contaminant on standing at room temperature. The data will be omitted here.

B. Diffusion of iodate into and internal adsorption by pre-formed calcium oxalate

The results to be described furnish good evidence for the existence of internal surface in open communication with the exterior of the crystals of calcium oxalate.

For the purpose of comparison, the results obtained with the precipitate formed in cold solution are presented; these results are neither distinctive nor conclusive, but lend greater weight to the conclusions drawn from the behavior of Hahn's precipitate (table 5). The precipitates were obtained by adding 20 cc. of ammonium oxalate to 24 cc. of calcium chloride, both 0.25 *N*, at room temperature. The time of addition was 1 minute. After the specified time of standing, 10 cc. of 0.050 *M* potassium iodate was added and the mixture shaken as indicated in table 3. To determine the amount of iodate which had gone into the interior of the crystals it was only necessary to add dilute hydrochloric acid (40 cc. of 0.1 *N* was used) and remove the liberated iodine with thiosulfate, then to add concentrated hydrochloric acid to dissolve all the precipitate and finally to titrate the iodine liberated by the iodate in the particles.

The reproducibility of these experiments is not particularly good. The anomalous results are explained by the existence of two opposing effects: diffusion into the crystal versus recrystallization and transformation of hydrates.

The next series of precipitates (table 4) was obtained from hot solution. Ten cubic centimeters of 0.25 *N* ammonium oxalate was added rapidly dropwise to a mixture of 50 cc. of water and 12 cc. of 0.25 *N* calcium chloride heated to 100°C. Twelve cubic centimeters more of calcium solution was then added to the main solution and again precipitated with 10 cc. of oxalate. This particular procedure was used to obtain crystals that would not be too small. The average crystal diameter was 0.5 to 1 micron. No recrystallization was apparent after a day, but it is not possible to say conclusively that none had taken place. The liquid containing the precipitate was cooled immediately after precipitation by cold water. Ten cubic centimeters of 0.050 *M* potassium iodate was added 5 minutes after the end of the precipitation. The amount of iodate that had permeated the crystals was determined in exactly the same manner as described above.

The variation in amount of post-occlusion with time is very regular. The effect of the aging of the crystals is well marked.

TABLE 3

Diffusion of iodate into and adsorption by calcium oxalate precipitated at room temperature

NO.	TIME OF STANDING BEFORE ADDITION OF IODATE	TIME OF SHAKING AFTER ADDITION OF IODATE	IODATE IN PRECIPITATE (CC. OF 0.0050 *N* THIOSULFATE)
1	0 minute	¼ minute	0.15
2	0 minute	1 minute	0.3; 0.45
3	0 minute	2 minutes	0.55
4	0 minute	5 minutes	0.7
5	0 minute	10 minutes	1.0; 1.4
6	0 minute	15 minutes	1.05; 1.1
7	0 minute	60 minutes	1.85
8	0 minute	180 minutes	1.7
9	0 minute	20 hours	4.7; 5.4
10	0 minute	48 hours	5.5; 7.1
11	0 minute	68 hours	8.5
12	5 minutes	15 minutes	0.55
13	10 minutes	15 minutes	0.35
14	15 minutes	15 minutes	0.25
15	30 minutes	15 minutes	0.20
16	60 minutes	15 minutes	0.15
17	80 minutes	100 minutes	0.25
18	200 minutes	24 hours	5.3
19	24 hours	29 hours	3.0
20	26 hours	3 days	0.3
21	48 hours	25 hours	0.5
22	2 days	5 days	0.6; 0.2
23	3 days	5 days	0.3

TABLE 4

Diffusion of iodate into calcium oxalate precipitated hot

TIME OF STANDING BEFORE ADDITION OF IODATE	TIME OF SHAKING AFTER ADDITION OF IODATE	IODATE IN PRECIPITATE (CC. OF 0.0050 *N* THIOSULFATE)
5 minutes	5 minutes	0.4
5 minutes	10 minutes	0.55
5 minutes	20 minutes	0.6
5 minutes	30 minutes	1.05
5 minutes	60 minutes	1.1
5 minutes	120 minutes	1.1
5 minutes	180 minutes	1.15
5 minutes	20 hours (not shaken)	1.85
1 hour	20 hours (not shaken)	1.0
1 hour	2 hours	0.9
2 hours	20 hours (not shaken)	0.85
20 hours	2 hours	0.4; 0.5
3 days	2 hours	0.3

Finally we have the behavior of Hahn's precipitate. Twenty cubic centimeters of oxalate and 21 cc. of calcium were added simultaneously to 50 cc. of water at room temperature, the calcium being kept 1 cc. in excess; time, 5 minutes. At the end of the precipitation, 3 cc. more of calcium chloride was added and immediately thereafter 10 cc. of 0.050 *M* potassium iodate; the mixture was then shaken (table 5). The internal iodate was determined as before.

These results are decisive. The particle size of Hahn's precipitate is large enough to preclude the possibility of any appreciable recrystallization on standing at room temperature. The diffusion of iodate into calcium oxalate is rapid at first and then falls off. More than 25 per cent of the total amount of iodate has entered the crystal 2 minutes after precipitation and 50 per cent after 10 minutes. The aging of the crystals has a very marked effect on the amount of iodate taken up. The permeability of the crystal has decreased to 50 per cent of the original after an hour or two. These effects quite definitely indicate that calcium oxalate crystals have a discontinuous structure and that they tend to perfect themselves on standing in solution.

TABLE 5

Diffusion of iodate into Hahn's precipitate formed cold

TIME OF STANDING BEFORE ADDITION OF IODATE	TIME OF SHAKING AFTER ADDITION OF IODATE	IODATE IN PRECIPITATE (CC. OF 0.0050 *N* THIOSULFATE)
0 minute	2 minutes	1.2
0 minute	5 minutes	1.5
0 minute	10 minutes	2.1
0 minute	30 minutes	2.4
0 minute	60 minutes	3.15
0 minute	2 hours	4.05
0 minute	21 hours	3.7
20 minutes	10 minutes	1.6
40 minutes	10 minutes	1.0
70 minutes	10 minutes	0.9
20 minutes	2 hours	2.7
40 minutes	2 hours	2.0
1 hour	2 hours	1.75
2 hours	2 hours	1.6
4 hours	2 hours	1.0
20 hours	2 hours	0.4
44 hours	2 hours	0.25

DISCUSSION OF THE RESULTS

1. Table 1 shows that calcium oxalate freshly precipitated at room temperature from fairly concentrated solutions loses fairly much occluded

iodate on aging; e.g., immediately after precipitation the amount of iodate corresponds to 14.2 cc. of 0.005 *N* thiosulfate, but after a few days equilibrium is reached, and the figure falls to 7.8. The case here is rather complicated, since the primary precipitate consists of the higher hydrates of calcium oxalate and these undergo transformation into the monohydrate on standing, accompanied by an entire structural change and recrystallization. Table 3 shows the pronounced porous character of calcium oxalate formed under the above conditions. The amount of iodate diffusing into, and being adsorbed at, the internal surface continually increases with the time of shaking and finally, after about two days, reaches a value almost identical with that found in calcium oxalate containing coprecipitated iodate, shaken for two days (see table 1).

From this behavior it is not justifiable to infer, however, that the processes of the effusion and diffusion are reversible, because other factors, such as transformation of higher hydrates with recrystallization, play a predominating rôle here. The figures in table 3 indicate that the changes take place within a short time after precipitation.

2. Table 2 shows the slow effusion of coprecipitated iodate from calcium oxalate prepared at room temperature according to F. L. Hahn's procedure. Although no recrystallization takes place here on aging, the iodate content has decreased to about half of its original value after two days. The reverse process, namely, the diffusion into, and adsorption of iodate by, the internal surface is demonstrated by the figures in table 5. The aging process takes place very rapidly. Comparison of the amount of iodate adsorbed at the internal surface after a day (table 5, 3.7 cc.) with the amount of coprecipitated iodate in the crystals after the same period (table 2, 24.6 cc.) indicates that on aging only a small part of the capillaries is filled by lattice ions, and that the "isolated internal surface" is fairly large. Actually most of the iodate coprecipitated is buried within the crystal and has no chance to escape.

3. Table 3 shows that calcium oxalate precipitated at 100°C. and allowed to stand at room temperature takes up only a very small amount of iodate. In agreement herewith it was found in the previous paper that calcium oxalate prepared under the above conditions loses hardly any coprecipitated iodate, if allowed to age at room temperature. Still the amount of coprecipitated iodate is fairly large (compare table 1 in previous paper (3)), thus showing that the "isolated internal surface" of calcium oxalate precipitated at 100°C. is fairly large and that the iodate is buried within the crystal. The internal surface in open communication with the outside is distinctly smaller than the same of a precipitate prepared at room temperature according to Hahn, even though the latter has a larger crystal size. (Compare tables 4 and 5.)

4. Summarizing, it appears that: (a) Coprecipitated ions quite gener-

ally are adsorbed at the internal surface. (b) A distinction is to be made between (1) internal surface in open communication with the exterior of the crystal, and (2) isolated internal surface. A freshly prepared precipitate very rapidly undergoes internal structural changes that result in an increase of the isolated internal surface and prevent any further effusion of coprecipitated material from within, or diffusion into, and adsorption of ions at its internal surface. The most effective purification of a precipitate is to be expected if the crystals by a slow dissolution and deposition process undergo an entire recrystallization. Calcium oxalate precipitated at 100°C. and aged at room temperature loses hardly any coprecipitated iodate, whereas an effective purification is achieved if the digestion is carried out at higher temperature for a longer time. Under the latter conditions a real recrystallization takes place.

II. PHENOMENA WITH POTASSIUM PERCHLORATE-PERMANGANATE

To confirm the interpretation of the phenomena described with calcium oxalate and potassium iodate, experiments of a similar nature were made with potassium perchlorate and potassium permanganate. The object of these experiments was to determine whether permanganate could diffuse into crystals of potassium perchlorate and be adsorbed internally. If fractures and discontinuities exist in a real crystal of potassium perchlorate, such a crystal placed in a saturated solution of potassium perchlorate containing dissolved potassium permanganate should become stained by the latter. Those two salts are strictly isomorphous and if the effect expected actually exists it should be plainly shown by this pair.

No detailed description of the experiments and the results will be given here—only the salient facts. It was found that crystals of C.P. potassium perchlorate immersed in a saturated solution of the same salt in 0.1 *N* potassium permanganate for a short time—an hour was sufficient—were colored distinctly pink after removal from this solution and after washing with a saturated solution of potassium perchlorate to remove adhering permanganate. Recrystallized potassium perchlorate obtained by evaporating a solution of the salt at room temperature also took up permanganate, but only slightly, so that the crystals were only faintly tinted. If the recrystallized perchlorate was ground in a mortar to give fragments 10 to 100 microns in diameter and these placed in permanganate as before, then it was found that so much potassium permanganate penetrated the crystals that they were colored a vivid red. The permanganate was actually in the interior of the crystals and not at or near the surface, as was proved by taking the colored crystals and shaking them with a volume of water insufficient to dissolve them all. The fragments remaining, though greatly reduced in size, were still colored. Even more drastic treatment failed to remove the color; the red crystals were shaken with a dilute solution of hydrochloric acid and hydrogen peroxide; after a week in this mixture the perchlorate was still strongly colored. Microscopic examination of the colored crystals in reflected light under low magnifications showed that they were homogeneously colored, although some fragments were more strongly colored than others. It is impossible that the coloration of the crystals can be due to permanganate seeping into microscopically visible cavities or cracks.

Beyond a manner of doubt, the permanganate has diffused into microscopically invisible breaks, faults, fractures, discontinuities, or capillaries in the lattice of the perchlorate and has been adsorbed at the internal surface. The phenomenon is not simply one of diffusion alone, for then any imperfect crystal would be colored by permanganate. This was found definitely not to be true. Thus, ground sodium chloride kept in permanganate for a long time remained perfectly uncolored except for an isolated particle or two which had been colored by permanganate that had penetrated into some microscopic crack or cavity. The coloration of a crystal appears to be dependent upon adsorption or incorporation of the colored substance in the lattice. Thus in the case of potassium perchlorate–permanganate, the permanganate, being isomorphous with the first-named salt, will tend to perfect the lattice of this crystal if given the opportunity to do so, i.e., a real crystal of potassium perchlorate immersed in permanganate will be colored by the latter as a consequence of the building up of the lattice. If this be the correct explanation, an imperfect crystal of potassium perchlorate allowed to stand in its own saturated solution should no longer be able to take up permanganate. This was verified. Ground crystals of perchlorate which became strongly colored if first placed in potassium permanganate would no longer take up this substance to more than a very slight extent if first immersed in a saturated solution of potassium perchlorate. The behavior is very striking. The explanation is obvious. When the imperfect crystals were kept in contact with saturated perchlorate, potassium and perchlorate diffused into the discontinuities and filled them by building up the lattice. Permanganate was therefore unable to color the crystals when they were later brought into contact with it. It is evident that crystals of perchlorate which have formed by slow evaporation and which have stood for some time in the saturated solution should take up but little permanganate as already described. Crushing the crystals of the salt should expose the openings of more internal surfaces. Therefore the ground crystals should be colored much more strongly, as was actually found. It is also possible that the stress of grinding causes more faults to appear in the lattice.

The first well authenticated instance of artificial coloration of a crystal appears to have been reported by Vater (4), who found that an artificial crystal of calcite immersed in Thoulet's liquid (a solution of mercuric iodide in potassium iodide) became colored yellowish-brown; the coloration was hastened by boiling the crystals with the solution. Cleavage fragments of Iceland spar became similarly colored. The coloring was entirely homogeneous; the crystals were pleochroic. The last observation is especially worth noting. If the crystals were immersed in water they became colorless after a time. The coloration of Vater's crystals was probably due to iodine.

Retgers (5) emphasized the extreme importance of these results. Strangely enough these observations of the permeability of crystals to solutions do not appear to have aroused much attention. The number of instances of artificial coloration of crystals has remained small.[1] Instances of permeability of crystals to gases are also known, for example, oxidation and change of color of olivine kept in the atmosphere. These facts all speak for a mosaic structure of real crystals.

III. PHENOMENA WITH BARIUM SULFATE–POTASSIUM PERMANGANATE

D. Balarew (2) found that freshly precipitated barium sulfate allowed to stand in potassium permanganate solution was able to take the latter substance into the crystals and give a colored precipitate; he also noted the effect of aging and drying. Such treatment diminished markedly the power of barium sulfate to become colored. Experiments of a similar nature have been made in this laboratory; they can be carried out in a very simple way and offer a striking demonstration of the secondary structural changes taking place in a fresh precipitate on aging. Freshly prepared barium sulfate shaken immediately after precipitation with a permanganate solution assumes a slightly pink color after a few minutes. The intensity of the latter—an indication of the amount of permanganate in the crystals—increases with time, and approaches a maximum after a day or two. Such a precipitate after washing is still red, and retains the color if shaken for a week or longer with a solution of hydrogen peroxide in strong hydrochloric acid. If the barium sulfate is allowed to stand after precipitation for some days and then treated with permanganate, hardly any of the latter compound is taken up, thus showing that the porous character has materially decreased or that most of the pores have been blocked by dams of barium sulfate.

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[1] Toward the end of the nineteenth century the European jewelers were alarmed by reports that yellowish diamonds were being transformed into clear colorless ones by immersion in solutions of blue dyestuffs. Retgers (5), who mentions this incident, regarded it as quite possible that the dye had actually diffused into the crystal in these cases and rendered the diamond colorless (blue and yellow being complementary colors). It appears improbable that a film of dye on the exterior could produce this effect. The alchemists were familiar with the decoloration of yellow diamonds by indigo solution (Ferrandus Imperatus, 1695). (See Janettaz: Bull. soc. min. 14, 65 (1893).)

It may be mentioned in conclusion that ground crystals of potassium sulfate kept in potassium chromate and potassium manganate solutions become faintly yellow and bluish-green respectively. A more thorough study of internal adsorption by crystals and of a secondary structural change taking place in a fresh precipitate is planned for the future.

SUMMARY

1. A fresh precipitate of calcium oxalate or barium sulfate prepared at room temperature forms very inhomogeneous crystals, showing a porous structure. Diffusion of solution into the capillaries followed by adsorption of solution at the internal surface takes place, if the adsorbent is added after the precipitation. Precipitates prepared at 100°C. show a similar behavior, but one not as pronounced as when obtained at room temperature from relatively concentrated solutions.

2. Freshly prepared precipitates on aging undergo rapid structural changes which result in an incomplete perfection of the crystals. Only a small part of the capillaries is entirely filled by the lattice material, most of them being blocked by the latter, thus isolating the internal surface from the outside. The *isolated internal surface* is much larger in a precipitate obtained from hot than from cold solutions.

3. Coprecipitated foreign substances in crystalline precipitates are adsorbed on the internal surface. A purification occurs on aging by effusion of part of the contaminants through the capillaries; the impurities at the *isolated internal surface*, however, cannot be expelled.

4. A slow recrystallization of a precipitate via the solution yields relatively perfect and pure crystals.

5. Most crystalline salts may be expected to have a relatively large isolated internal surface. The latter can be partly exposed by grinding the crystals to smaller dimensions.

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THE INFLUENCE OF COMBINED OXYGEN ON THE DETERMINATION OF VAPOR ISOTHERMALS ON POROUS SOLIDS. II

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INTRODUCTION

As a result of the investigation carried out on charcoal (1), it was decided to employ silica gel to see if the step-like structure of the isothermal could also be obtained in this case by the modified static technique. The apparatus and general methods used were identical with those in the previous paper, except that the evacuation was carried out at 110°C. A further slight alteration in technique was also necessary, since carbon tetrachloride and water vapors (displaced from the gel) cannot be satisfactorily separated by a refrigerant. It was found also that when carbon tetrachloride was heated to 100°C. in the closed container it reacted with the water in the gel, giving rise to phosgene and hydrochloric acid. The container was charged and heated to 100°C. with the tap closed as before and then opened with liquid air on the freezer and as much vapor drawn off as possible. This was pumped away and the gel charged with a fresh sample of carbon tetrachloride. In this way displaced water, hydrochloric acid, and phosgene were removed. It was realized that this form of flushing out might be too drastic in the present case, thereby causing the gel to deteriorate. The water in the unevacuated gel will be held in two ways, partly as adsorbed vapor and partly as a constituent of the gel structure. Admittedly the two forms merge, since the adsorbed molecules which are directly attached to the active centers must be so strongly held that they may be considered to be quasi-chemically attached and therefore similar to the structural water. If the carbon tetrachloride reacts with the structural water it will cause the gel to deteriorate, but if it only reacts with the adsorbed water, it will cause a cleaning-up of the surface, thereby increasing the capacity of the gel.

In any case the adsorbed water will be driven off and that is the first object of this investigation—the attainment of a surface free from foreign adsorbed matter.

EXPERIMENTAL

Carbon tetrachloride isothermals on silica gel at 25°C.

A sample of just over 6 g. of gel was evacuated at 110°C. to a pressure of 9×10^{-4} mm. It was then charged with carbon tetrachloride at 100 mm. pressure, the container tap closed, and the vessel heated at 60°C. for three hours. The container was then opened with liquid air on the freezer and as much vapor as possible removed. This was pumped away and the container recharged at 50 mm. The same procedure was adopted as before and it was again charged at approximately 4 mm. at 25°C., the initial quantity of carbon tetrachloride adsorbed being 150.6 mg. per gram. The isothermal consisted of a desorption curve, followed by resorption to a much higher pressure than previously and further desorption, and is shown in figure 1.

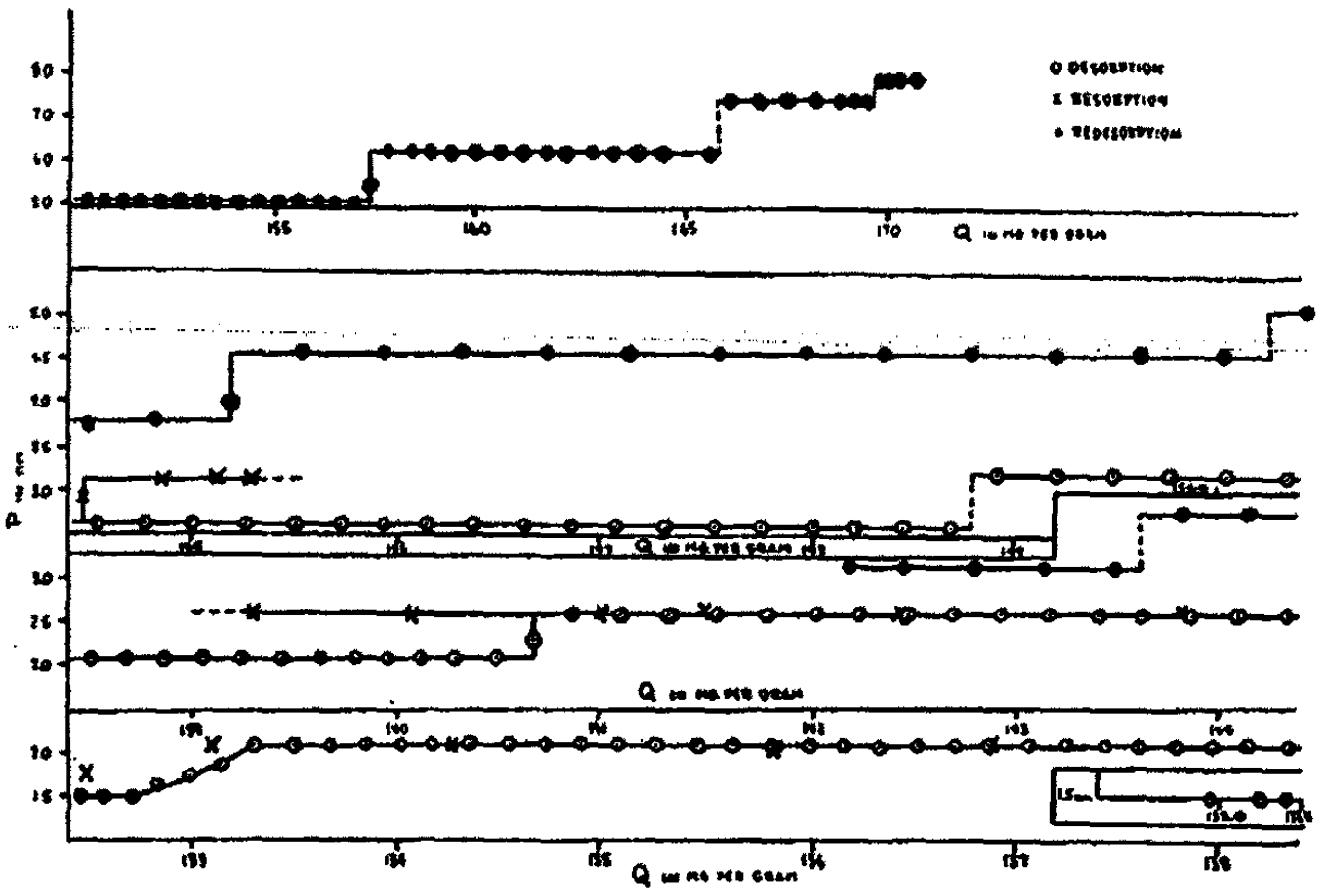

FIG. 1

The complete isothermal comprises 175 points taken over a pressure range of 7 mm. The agreement between the calculated quantity values and those obtained by weighing is good.

Calculated quantity	*Quantity by weight*
145.27 mg. per gram	145.3 mg. per gram
142.18 mg. per gram	141.8 mg. per gram

Equilibrium was almost as rapid as in the experiment on charcoal (1) in the case of desorption, but sorption was definitely slower, taking a quarter of an hour to reach equilibrium, after which no change was observed after standing for twenty hours.

The isothermal was not found to be reproducible, although the pressures at which the breaks occur remained the same, whether on sorption or desorption curves. With successive sorptions or desorptions, the quantity for any given pressure decreases, the gel thus becoming definitely poorer for carbon tetrachloride. From this it would appear that the latter is continuously removing water from the gel, including some of the structural water. This will be dealt with later in the discussion of the benzene isothermals. A few points were determined at lower quantity values to ascertain the pressures at which the breaks occur. The values for the latter in the different series are given in table 1, together with those obtained by the modified retentivity technique.

TABLE 1

Pressures (in millimeters) at which the breaks occur

STATIC			MODIFIED RETENTIVITY
Desorption	Resorption	Redesorption	
		7.96	
		7.44	
		6.28	
		5.10	
		4.60	4.61
		3.78	3.77
3.19	3.13	3.14	3.15
2.59	2.62	2.56	2.64
2.08	2.07	2.08	2.06
1.50		1.51	1.45
		1.18	1.14

The agreement in all cases is good, especially in view of the fact that for the final desorption curve of the static experiment, the gel was charged to 50 mm., whereas in the retentivity experiment it was charged at 8.4 mm. The quantity of vapor adsorbed at 50 mm. was 170.7 mg. per gram. The sequence of breaks has been plotted against the pressures at which they occur (figure 2). As will be seen, a smooth curve results within experimental error. In figure 3 comparison is made with an isothermal determined by the modified retentivity technique and one obtained by the static technique without employing any flushing of the gel, the individual points being plotted in the latter case only.

The latter was carried out some years ago and it was concluded that the isothermal gave a smooth reversible curve. It was seen, however, by comparison with the later retentivity work, that the whole range covered corresponded to a vertical portion of the isothermal. In each case the initial charging pressure was the same. In view of this result it was deemed advisable to repeat the benzene isothermal by the new static technique.

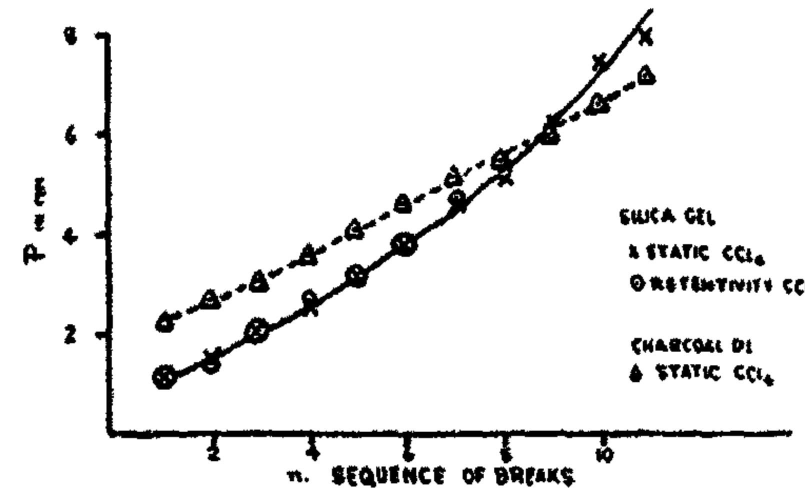

FIG. 2

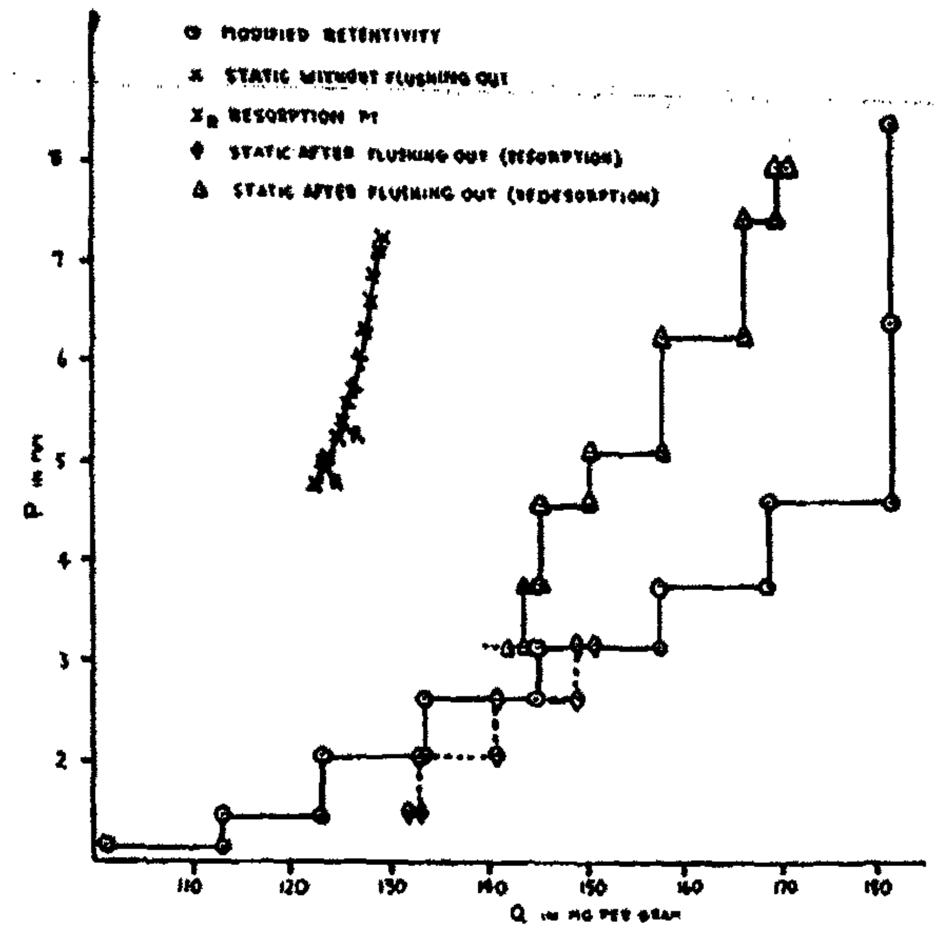

FIG. 3

Benzene isothermals on silica gel at 25°C.

Seven and four-tenths grams of gel was evacuated to 1×10^{-3} mm. at 110°C. and charged to 42 mm. pressure at room temperature. The tap was closed and the gel heated to 50°C. for two hours. It was then opened with liquid air on the freezer and as much benzene and water removed as was possible. This was pumped away and the gel recharged to 50 mm. pressure, and the container heated at 230°C. for three hours with the tap shut as before. It was then opened with liquid air on the freezer and as much vapor removed as was possible. The gel was now charged at 10.1 mm. and a desorption isothermal carried out. (Figures 4 A and 5 A.)

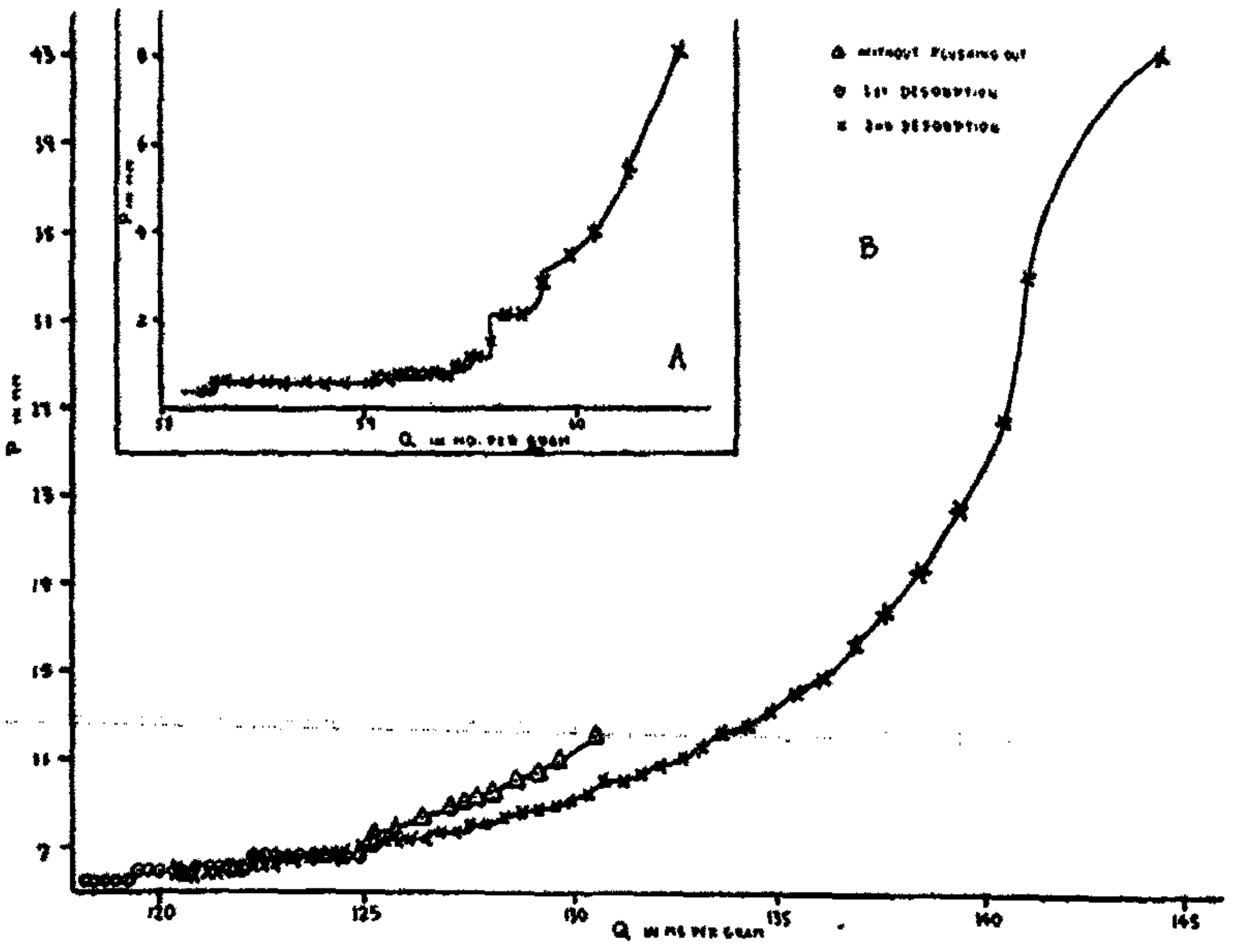

Fig. 4

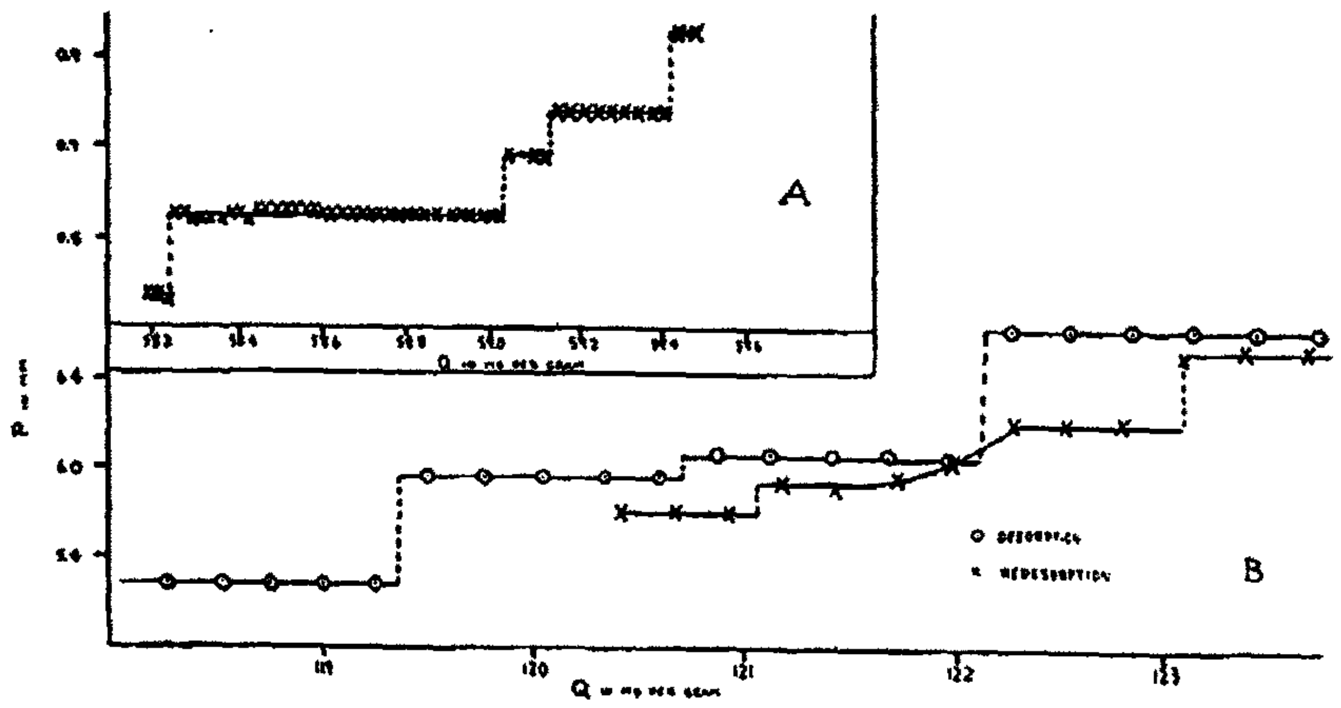

Fig. 5

The initial quantity sorbed was 60.9 mg. per gram and the final 58.2 mg. per gram (58.19 by pressure change method). Reference to figure 5 A shows the isothermal to be quite definitely rectangular in shape.

A second sample of gel (6.56 g.) was evacuated to 8×10^{-4} mm. at 110°C. and charged at room temperature to 20 mm. The tap was then shut and the temperature raised to 100°C. for two hours. All vapor was removed as in the previous case and the gel recharged to 50 mm., the initial quantity being 125.6 mg. per gram. A desorption isothermal was carried out, the final quantity being 117.5 mg. per gram (118.01 by the pressure change method). The gel was then recharged to 50 mm., the quantity adsorbed being 145.4 mg. per gram, and a desorption isothermal carried out to 119.3 mg. per gram (120.39 by pressure change method). Reference to figure 5 B shows that the steps in the first desorption isothermal are very well defined, whereas they are not quite so definite in the second desorption, although they are undoubtedly present. Insufficient points were taken at higher pressures to identify the breaks, but the curve is definitely discontinuous. In figure 4 B, the previous results (2), which employed no flushing out technique, have been added and it shows that the differences between the isothermals are small at low pressures. The fact that the breaks are not so well defined on the final desorption isothermal is of interest, since equilibrium was not established so rapidly on this curve as in other cases. Previously this fact has been definitely connected with an unclean surface, and thus it would seem that more water has been turned out of the gel by the high pressure charge. This is borne out by the fact that the gel has slightly improved as regards its capacity for benzene. The isothermal of the gel which was flushed out at 230°C. shows that this treatment has been too drastic and the gel has deteriorated. It has been shown (Part I of this series and the present paper) that flushing out at 100°C. gives similar results, whether the charcoal has been previously evacuated to 110° or 800°C. Thus, the effect of flushing out the gel at 230°C. would probably correspond to an evacuation temperature of over 1000°C., and the gel would most certainly break down under these conditions.

A comparison of the effect of recharging on the carbon tetrachloride and benzene isothermals shows that the former is a much more powerful agent for the removal of water from the gel. On recharging with benzene a definite cleaning-up effect was observed, whereas with carbon tetrachloride successive recharges caused the capacity of the gel to lessen. In all these experiments on silica gel the equilibrium has not been established quite so rapidly as on a clean charcoal surface. The reason is obvious, since one can never remove all the water from the gel, hence one can only obtain rectangular breaks on successive sorption and desorption isothermals when it is actually the structural water which is being removed, causing the capacity of the gel to lessen for the given vapor.

Thus isothermals on silica gel cannot be obtained as accurately as those on charcoal, since the surface is never entirely free from foreign adsorbed vapor unless water is the vapor whose isothermal is under determination.

Carbon tetrachloride isothermal on charcoal at 25°C.

A further experiment was carried out with carbon tetrachloride on Charcoal D1 (2) to see whether the C_xO_y, which (Part I) had been removed by 800°C. evacuation followed by flushing with vapor, could be removed by 110°C. evacuation and flushing in a manner similar to the previous experiments with silica gel. Approximately 4 g. of charcoal were evacuated in the usual manner till a pressure of 8×10^{-4} mm. at 110°C. was reached. The evacuated charcoal was then charged with carbon tetrachloride to a pressure of 54 mm. and heated to 50°C. with the container tap closed. This was allowed to cool overnight. After eighteen hours the container was heated to 110°C. for two hours and opened to liquid air for one hour, 30.53 mm. of carbon dioxide being evolved. This carbon dioxide, which was measured by placing melting methylcyclohexane on the freezer, was pumped away and the carbon tetrachloride allowed to stream back on the cool charcoal.

TABLE 2

Carbon tetrachloride isothermal on charcoal

P	*Q*	*P*	*Q*
mm.	*mg. per gram*	*mm.*	*mg. per gram*
7.14	307.14	4.10	296.39
7.15	306.18	3.54	295.92
6.60	305.29	3.54	295.45
6.60	304.40	3.54	294.98
6.00	303.59	3.08	294.57
6.00	302.78	3.06	294.16
5.48	302.04	3.02	293.76
5.48	301.30	72 hours rest	
5.18	300.60	3.02	293.36
5.18	299.90	2.62	293.01
4.58	299.28	24 hours rest	
4.58	298.66	2.62	292.66
4.58	298.04	2.62	292.31
4.10	297.49	2.62	291.96
4.10	296.94	2.28	291.66
		2.28	291.36

The container tap was shut and the pressure raised to 100°C. for two hours. The same procedure was adopted as in the previous case, 11.04 mm. of carbon dioxide being evolved. This was pumped away and the carbon tetrachloride allowed to stream back. The container was now heated to 120°C. for two hours, 1×10^{-2} mm. of carbon dioxide being evolved. A total of 41.6 mm. of carbon dioxide has thus been displaced by the carbon tetrachloride after evacuation to 8×10^{-4} mm. at 110°C., as compared with a total of 14 mm. of combined oxygen after evacuation to 2×10^{-3} mm. at 800°C. The initial quantity of carbon tetrachloride adsorbed was 308.1 mg. per gram. The isothermal consisted of a single desorption curve and the results are given in table 2.

The quantity value by weight = 291.7 mg. per gram, which agrees with that found by the pressure change method.

It is obvious from the figures that the isothermal consists of a series of steps in just the same way as the isothermal on the 800°C. evacuated charcoal.

Equilibrium was almost instantaneous, similar to when carrying out the carbon tetrachloride isothermal on silica gel. In the 800°C. evacuated isothermal the quantity adsorbed at 5.24 mm. was 266.9 mg. per gram, whereas in the present case the quantity is 301.0 mg. per gram. This is the type of agreement one obtains at lower pressures with two samples of an underactivated charcoal, this difference tending to lessen at higher pressures. Two samples of charcoal A (3) charged at 33 mm. with carbon tetrachloride at 15°C. gave the following figures after drift had been overcome: sample 1, 337.3 mg. per gram; sample 2, 312.5 mg. per gram.

TABLE 3

Pressures (in millimeters) at which the steps occur

110°C. EVACUATION	800°C. EVACUATION	
	1st desorption	2nd desorption
7.14		
6.60		
6.00		
5.48		
5.18	5.24	
4.58	4.70	4.71
4.10	4.12	4.12
3.54	3.57	3.56
3.02	3.02	3.07
2.62		2.60
2.28		2.34

A comparison of the pressures at which the steps occur has been made in table 3.

DISCUSSION

Fair agreement has been obtained between the 110°C. and 800°C. evacuation isothermals, showing that either method is effective for removing the C_xO_y. The sequence of the breaks against the pressures for the 110°C. isothermal has been plotted in figure 2.

In view of the many ways in which carbon dioxide has been found to affect the determination of isothermals on charcoal, and water to affect those on silica gel, it appeared advantageous to collect some of these data and present them in the present paper.

In all previous work, the isothermals represent poisoned and not true isothermals. This is most serious in those cases where authors have not adopted any flushing method and particularly so when the original evacuation has been carried out at low temperatures. It is not so serious if the original temperature of evacuation was high, but, even so, the poisoning effect is still present. One can, however, get apparent reproducibility in many cases, but the fact that the isothermal is nevertheless poisoned is demonstrated by the increase of quantity adsorbed in a carbon tetrachloride isothermal after 800°C. evacuation, when compared with one evacuated at 110°C., when using a highly activated charcoal.

A further instance of this (2) was noticed with a water isothermal on Charcoal B (3). Here the isothermal was apparently reversible until the original charging pressure was exceeded, when carbon dioxide was evolved and the isothermal showed that drift had taken place. An isothermal showing further instances of this will be given in Part III of this series.

In this connection a very serious criticism may be made regarding almost all previous static experiments, in that no attempt has been made to separate the vapor concerned from the carbon dioxide and carbon monoxide evolved from the surface of the charcoal, or water from the silica gel. However well the surface may have been evacuated, considerable quantities of gas are evolved from the surface by the action of the vapor whose isothermal is under determination. The author has found 2 mm. of carbon dioxide to be present in the vapor phase after saturating charcoal at a pressure of 16 mm. of water vapor. Considerable quantities have been noted in other cases also (2). It is of interest to mention the extraordinary cleaning-up effect noted in the same paper with amyl alcohol, where a slightly higher charge raised the quantity adsorbed from 133 mg. per gram to 396 mg. per gram. Similar instances have been noted in a recent paper[1] on the sorption of vapors by unactivated charcoal. Again carbon dioxide or the C_xO_y, has been found to exert a very serious influence on both the number and pressures of the breaks. In many instances the pressure of a given break is raised, while in other cases extra breaks are added owing to the presence of carbon dioxide on the charcoal surface. In all cases the resultant isothermals consist of a series of curves until the surface is clean, when rectangular steps will result (Part I of this series). An indication that the surface of the adsorbing body is clean is given by the adsorption being instantaneous whether during sorption or desorption. The same

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[1] Submitted to the Transactions of the Faraday Society for publication.

applies if one is freezing out a constituent vapor from a mixture, equilibrium being slow, but if the gas is a pure substance, then equilibrium is instantaneous.

SUMMARY

The effect of flushing out with vapor has been noted in isothermals on silica gel.

The change in the position of the isothermals on recharging with vapor has been examined.

The pressures at which breaks occur in isothermals on silica gel determined by the modified retentivity and static techniques have been compared.

The resultant isothermal, after flushing out a charcoal which had been evacuated at 110°C., has been compared with one evacuated at 800°C. and the pressures at which the breaks occur have been tabulated.

Some effects of carbon dioxide on the determination of isothermals have been noted.

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FORMATION OF SUGARS IN MIXTURES OF TARTARIC ACID AND ALDEHYDES IN TROPICAL SUNLIGHT

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It is well-known from the work of Usher and Priestly (1), and Baly and coworkers (2) that carbon dioxide and moisture under the influence of light are converted into formaldehyde. Moore and Webster (3) claimed to have obtained formaldehyde by exposing solutions of colloidal uranic hydroxide through which carbon dioxide was passed. Dhar and Sanyal (4), and Gopalrao and Dhar (5) have made extensive investigations on this point and established the formation of formaldehyde from water and carbon dioxide under the influence of light and photosensitizers, such as chlorophyll, ferric chloride, zinc oxide, methylene blue, methyl orange etc.

The conversion of formaldehyde to sugars under the influence of light has been reported by Baly and coworkers (2), Dhar and Sanyal (4), and Gopalrao and Dhar (5).

That some of the aliphatic acids, such as tartaric, acetic, and oxalic acid and others, decompose in the presence of light and give carbon dioxide is also known from the work of Ciamician and Silber (6), Pierce and Morey (7), and others.

It occurred to the author that in such cases the carbon dioxide molecule, just at the time of its liberation from the acid molecule, might be in a more reactive condition than the ordinary carbon dioxide molecule, and in the presence of strong illumination might easily be converted into sugars, without the aid of any photocatalyst.

The results obtained in an investigation carried out with a view to test the above idea are embodied in the present paper.

EXPERIMENTAL

Aqueous solutions of tartaric acid, aldehydes, alcohols, and mixtures of tartaric acid with aldehydes or alcohols were exposed to sunlight with and without photosensitizers in sealed tubes of soft glass, Pyrex conical flasks covered with beakers, and quartz vessels. Portions of the same solutions were kept in bulbs and conical flasks also in the dark. The solutions exposed and unexposed were examined periodically and simultaneously.

Benedict's[1] solution was used to test sugars, as Fehling's solution is also reduced by formaldehyde. In the experiments carried out in darkness no sugar formation was detected.

TABLE 1

EXPERIMENTS	TIME OF EXPOSURE	RESULTS
	hours	
1. Tartaric acid alone	15	No sugar detected
* Tartaric acid alone	125	No sugar detected
2. Tartaric acid + zinc oxide	15	No sugar detected
3. Tartaric acid + ferrous sulfate	15	No sugar detected
4. Tartaric acid + sodium bicarbonate	100	No sugar detected

TABLE 2

EXPERIMENTS	TIME OF EXPOSURE	RESULTS
	hours	
1. Formaldehyde alone	15	Formic acid detected; no sugar
* Formaldehyde alone	125	Formic acid detected; no sugar
2. Formaldehyde + zinc oxide	15	Formic acid detected; no sugar
* Formaldehyde + zinc oxide	125	Formic acid detected; no sugar
3. Formaldehyde + calcium carbonate	15	No sugar detected
4. Formaldehyde + magnesium carbonate	15	No sugar detected
5. Formaldehyde + zirconium nitrate	30	No sugar detected
6. Formaldehyde + cupric nitrate	30	No sugar detected
7. Formaldehyde + sodium hydroxide	30	No sugar detected
8. Formaldehyde + dilute sulfuric acid	30	No sugar detected
9. Formaldehyde + magnesium nitrate	30	No sugar detected
10. Formaldehyde + tartaric acid	84	Presence of sugar detected
* Formaldehyde + tartaric acid	100	Presence of sugar detected

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[1] In this paper, wherever it has been observed that Benedict's solution is reduced, it has been inferred that reducing sugars are formed. One of the possible objections against this inference may be that in such cases we might actually be dealing with reducing agents which are not sugars. Dhar and Sanyal (J. Phys. Chem. **29**, 926 (1925)), Gopalrao and Dhar (Ibid. **35**, 1426 (1931)) observed that whatever may be the behavior of Fehling's solution, Benedict's solution is not reduced by aldehydes. Baly, Heilbron, and Barker (J. Chem. Soc. **119**, 1028 (1921)) reported having obtained tests with Benedict's solution which indicate the formation of sugar being equivalent in reducing power to 0.04 g. of glucose. A large number of experiments carried out by the author also lead to the same conclusion. It appears therefore to be quite safe to conclude that the reducing substances formed in experiments reported in this paper are reducing sugars.

The glass bulbs, conical flasks, and quartz vessels were carefully cleaned with hot chromic acid mixture and washed several times with distilled and finally with conductivity water. The solution of tartaric acid was prepared in conductivity water after boiling vigorously and it was kept in a stoppered Jena glass bottle. The other solutions were also made in conductivity water.

TABLE 3

EXPERIMENTS	TIME OF EXPOSURE	RESULTS
	hours	
1. Acetaldehyde alone	84	No sugar detected
* Acetaldehyde alone	125	No sugar detected
2. Acetaldehyde + zinc oxide	10	No sugar detected
* Acetaldehyde + zinc oxide	125	No sugar detected
3. Acetaldehyde + potassium nitrate	30	No sugar detected
* Acetaldehyde + potassium nitrate	125	No nitrite detected
4. Acetaldehyde + magnesium nitrate	125	No nitrite detected
5. Acetaldehyde + tartaric acid	84	Presence of sugar detected
* Acetaldehyde + tartaric acid	100	Presence of sugar detected

TABLE 4

EXPERIMENTS	TIME OF EXPOSURE	RESULTS
	hours	
1. Butyl alcohol alone	28	No sugar detected
2. Butyl alcohol + zinc oxide	28	No sugar detected
3. Butyl alcohol + tartaric acid	47	Presence of sugar detected
4. Amyl alcohol alone	28	No sugar detected
* Amyl alcohol alone	125	No sugar detected
5. Amyl alcohol + zinc oxide	28	No sugar detected
* Amyl alcohol + zinc oxide	100	No sugar detected
6. Amyl alcohol + potassium nitrate	100	No sugar detected
7. Amyl alcohol + magnesium nitrate	100	No sugar detected
8. Amyl alcohol + tartaric acid	47	Presence of sugar detected
* Amyl alcohol + tartaric acid	100	Presence of sugar detected
9. Ethyl alcohol alone	28	No sugar detected
10. Ethyl alcohol + tartaric acid	24	Presence of sugar detected

The tubes and flasks were exposed to the sun for periods varying from fifteen to eighty-four hours over several days (see tables 1 to 4). Some of the experiments marked with asterisks were repeated and the period of exposure was extended up to one hundred and twenty-five hours to ensure accuracy.

Equimolar solutions of tartaric acid, formaldehyde, butyl alcohol, and amyl alcohol were prepared in conductivity water. One hundred cubic centimeters of the solution of tartaric acid was mixed with 100 cc. each of the formaldehyde, butyl alcohol, and amyl alcohol solutions, respectively. The mixtures were exposed to the sun in quartz vessels for a period of forty hours.

The different mixtures were then titrated with Benedict's solution standardized with glucose solution (0.4294 g. per liter) with usual precautions. The results are given in table 5.

TABLE 5

BENEDICT'S SOLUTION		EQUIMOLAR MIXTURES EXPOSED IN QUARTZ VESSELS
1 cc.	≡	7.5 cc. of (amyl alcohol + tartaric acid in mixture)
1 cc.	≡	9.4 cc. of (formaldehyde + tartaric acid in mixture)
1 cc.	≡	14.8 cc. of (butyl alcohol + tartaric acid in mixture)
5 cc.	≡	7.0 cc. of glucose solution (0.4294 g. per liter)

DISCUSSION OF RESULTS

From tables 1, 2, 3, and 4 it is clear that there is no production of reducing sugars when aqueous solutions of tartaric acid, formaldehyde, acetaldehyde, and alcohols are exposed alone and with photosensitizing agents such as zinc oxide, ferrous sulfate, zirconium nitrate, cupric nitrate, etc.

Sugars are found to be formed only in mixtures of tartaric acid with aldehydes or alcohols.

Table 5 contains the results of semiquantitative experiments carried out.

The reactivity of the nascent carbon dioxide has been reported recently by Rajwansi and Dhar (8) in the formation of formaldehyde by exposing an aqueous solution of sodium bicarbonate.

The absence of sugars in aqueous solutions of tartaric acid or formaldehyde, and the presence of reducing sugars detected in the mixtures of tartaric acid and formaldehyde suggests that by virtue of the reducing properties of the aldehydes the nascent carbon dioxide formed during the decomposition of tartaric acid under the influence of light is reduced to carbon monoxide according to the equation:

$$CO_2 + HCHO = 2CO + H_2O$$

That ultra-violet light converts carbon dioxide to carbon monoxide is shown by Herchefinkel (9) and later by Coehn and collaborators (10).

It is reported by Berthelot and Gaudechon (11) that the presence of reducing substances facilitates the reaction $CO_2 \rightleftarrows CO + O$. Gopalrao and Dhar (reference 5, Part I) have also stated that such a decomposition takes place in visible light in presence of methylene blue or chlorophyll. The nascent carbon monoxide thus formed, owing to the reduction of carbon dioxide by aldehydes, reacts with water giving formaldehyde, and this nascent formaldehyde is polymerized to sugars. This explanation can be supported by the schemes of photosynthesis of sugars formulated by Heilbron (12) and Gopalrao and Dhar (reference 5, Part II). They emphasize the reactivity of the nascent state of formaldehyde for the formation of sugars.

During the experiments the alcohols are slightly oxidized to aldehydes, and the aldehydes thus formed explain the formation of sugars in the mixtures of tartaric acid and alcohols.

SUMMARY

(1). Aqueous solutions of tartaric acid and mixtures of tartaric acid with aldehydes or alcohols were exposed to tropical sunlight for varying periods of time.

(2). In solutions containing tartaric acid or formaldehyde only, no trace of sugar could be detected even after very long exposure.

(3). Sugar formation has been detected in mixtures of tartaric acid and aldehydes or alcohols.

(4). The probable rôle of the aldehydes has been suggested.

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THE VELOCITY OF BROMINATION OF ACETOACETIC ETHYL ESTER. I

THE WATER REACTION

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The object of this work was to make a contribution to the theory of prototropic reactions, and with this end in view it was decided to study the enolization of acetoacetic ethyl ester by measuring the rate of bromination. In aqueous solution the equilibrium

$$CH_3COCH_2COOC_2H_5 \rightleftarrows CH_3COH{:}CHCOOC_2H_5$$

is displaced mainly in favor of the ketone, the concentration of enol being only 0.4 per cent of the total concentration of the ester.

It is well known that bromine reacts practically instantaneously with the enol, while it does not affect the ketone appreciably. This fact is used in Meyer's (1) method for estimating the enol content of the equilibrium mixture by titration with bromine water. If bromine is added to an aqueous solution of acetoacetic ester, the enol is removed by the bromine as soon as it is formed. Therefore, in the amount of bromine used we have a measure of the progress of enolization.

A similar mechanism was first suggested by Lapworth (2) for the reaction between acetone and halogen in aqueous solution. Here the rate of halogenation is a measure of the velocity of enolization of acetone. In agreement with this explanation Lapworth found that the velocity was independent of the concentration and the nature of the halogen.

The kinetic experiments on the reaction of acetoacetic ester and bromine described in this paper agree with the following explanation. The reaction takes place in four steps:

$$CH_3COCH_2COOC_2H_5 \rightarrow CH_3COH{:}CHCOOC_2H_5 \tag{1a}$$

$$CH_3COH{:}CHCOOC_2H_5 + Br_2 \rightarrow CH_3COCHBrCOOC_2H_5 + H^+ + Br^- \tag{1b}$$

$$CH_3COCHBrCOOC_2H_5 \rightarrow CH_3COH{:}CBrCOOC_2H_5 \tag{1c}$$

$$CH_3COH{:}CBrCOOC_2H_5 + Br_2 \rightarrow CH_3COCBr_2COOC_2H_5 + H^+ + Br^- \tag{1d}$$

Thus the reaction does not stop when α-monobromoacetoacetic ester is formed, but this substance takes up more bromine giving the final product α,α-dibromoacetoacetic ester. The rates of bromination of the enol forms of acetoacetic ester (1b) and of monobromoacetoacetic ester (1d) are so great compared with the rates of enolization of the keto forms, that the reactions 1a and 1c determine the velocity of the total reaction. In agreement with this the concentration of bromine was always found to be without influence on the velocity of bromination.

From these assumptions we shall now deduce a mathematical expression for the amount of bromine used by the reaction t minutes after its start. We use the following symbols:

HR = keto form of acetoacetic ester,
HR′ = keto form of α-monobromoacetoacetic ester,
R″ = α,α-dibromoacetoacetic ester,
c = initial concentration of acetoacetic ester (ketone and enol),
ϵ = degree of enolization at keto-enol equilibrium,
t = time in minutes from the start of the reaction,
x = bromine used at the time t in equivalents per liter,
k_0 = unimolecular velocity constant for the enolization of HR (with no added catalyst),
h_0 = the same for HR′, and
r = h_0/k_0.
* By an asterisk we denote that the velocity constant has been calculated by means of decadic logarithms. Thus $k^* = 0.4343\,k$.

The enol concentration being always 0 after the start of the reaction, we have

$$(\mathrm{HR}) + (\mathrm{HR'}) + (\mathrm{R''}) = c \tag{2}$$

From equations 1a to 1d it follows that the bromine used by the reaction is

$$2(\mathrm{HR'}) + 4(\mathrm{R''}) = x \tag{3}$$

From equations 2 and 3 we have

$$(\mathrm{HR}) + \tfrac{1}{2}(\mathrm{HR'}) = c - \frac{x}{4} \tag{4}$$

The velocity of the consecutive reactions HR → HR′ → R″ is determined by the differential equations

$$-\frac{d(\mathrm{HR})}{dt} = k_0(\mathrm{HR}) \tag{5}$$

and

$$\frac{d(\mathrm{HR'})}{dt} = k_0(\mathrm{HR}) - h_0(\mathrm{HR'}) \tag{6}$$

At the time $t = 0$ we have

$$(\mathrm{HR}) = c(1-\epsilon) \quad \text{and} \quad (\mathrm{HR}') = c\epsilon \tag{7}$$

Integrating equation 5 and using equation 7 we obtain

$$(\mathrm{HR}) = c(1-\epsilon)\, e^{-k_0t} \tag{8}$$

From equations 5 and 6, together with the abbreviation $r = h_0/k_0$, we get

$$\frac{d(\mathrm{HR}')}{d(\mathrm{HR})} = r\frac{(\mathrm{HR}')}{(\mathrm{HR})} - 1 \tag{9}$$

Integrating equation 9 and using equation 7 we get (except when $r = 1$)

$$\frac{(\mathrm{HR}')}{(\mathrm{HR})} = \frac{1}{r-1} + \frac{1-r\epsilon}{(1-r)\,(1-\epsilon)^r}\left(\frac{(\mathrm{HR})}{c}\right)^{r-1} \tag{10}$$

(HR) and (HR′) are now eliminated from equations 4, 8, and 10:

$$\frac{c-\frac{x}{4}}{c} = Ae^{-k_0t} - \left(A - 1 + \frac{\epsilon}{2}\right)e^{-h_0t} \tag{11}$$

where we have used the abbreviation

$$A \equiv (1-\epsilon)\left(1 + \frac{1}{2(r-1)}\right). \tag{12}$$

Equation 11 may be written in the following way:

$$\frac{c-\frac{x}{4}}{c} = A\,10^{-k_0't} - \left(A - 1 + \frac{\epsilon}{2}\right)10^{-h_0't} \tag{13}$$

For special values of r the two-membered exponential expression 11 is reduced to a single-membered one. Thus,

$$\text{if } r = \infty, \qquad \frac{c-\frac{x}{4}}{c} = (1-\epsilon)e^{-k_0t} \tag{14}$$

$$\text{if } r = 1, \qquad \frac{c-\frac{x}{4}}{c} = \left(1 - \frac{\epsilon}{2} + \frac{1-\epsilon}{2}k_0t\right)e^{-k_0t} \tag{15}$$

$$\text{if } r = \tfrac{1}{2}, \qquad \frac{c-\frac{x}{4}}{c} = \left(1 - \frac{\epsilon}{2}\right)e^{-\frac{1}{2}k_0t} \tag{16}$$

$$\text{if } r = 0, \qquad \frac{c-\frac{x}{2}}{c} = (1-\epsilon)e^{-k_0t} \tag{17}$$

In order to show that the kinetic experiments agree with the explanation given above we find such values of the constants ϵ, k_0^* and h_0^* that the experimental values of x and t satisfy equation 13.

At first ϵ is determined. When t is small, equation 13, or the identical equation 11, may be written

$$\frac{c-\frac{x}{4}}{c} = A(1-k_0t) - \left(A-1+\frac{\epsilon}{2}\right)(1-h_0t) = 1-\frac{\epsilon}{2} - t\frac{k_0}{2}(1+(r-1)\epsilon) \qquad (18)$$

Consequently, ϵ can be computed by plotting $\frac{c-\frac{x}{4}}{c}$ against t for small values of t and rectilinear extrapolation to $t = 0$.

It is more difficult to determine k_0^* and h_0^*. If $h_0^* >> k_0^*$, the second exponential member of equation 13 will decrease rapidly for increasing values of t and will soon be negligible. If we plot $\log \frac{c-\frac{x}{4}}{c}$ against t we should get a curve which approaches asymptotically to a straight line with the slope $-k_0^*$ and makes an intercept $\log A$ on the ordinate axis. From these constants we easily get h_0^* by means of equation 12. In order to test whether all the experimental pairs of values of x and t agree with equation 13 for the values of the constants thus computed we plot

$$\log\left[\frac{c-\frac{x}{4}}{c} + \left(A-1+\frac{\epsilon}{2}\right)10^{-h_0^*t}\right]$$

against t. Now, all the points should fall on the straight line previously drawn. If there should be any systematic deviation we may attempt to obtain a better agreement by drawing a new straight line and repeating the operation.

The method here outlined is only applicable when h_0^* is much greater than k_0^*. If they are of the same order of magnitude, the curve will not sufficiently quickly approach a straight line. The following method can be used in all cases. For each pair of values of x and t found by experiment and for a series of values of r we calculate by the method of trial and error the values of k_0^* which satisfy equation 13. Thus, for each pair of x and t a curve through corresponding values of k_0^* and r is determined. We get a family of curves all going through the same point. The coördinates of this point are the values of k_0^* and r which satisfy equation 13 for all the experimental values (figure 1). Actually, we do not find a single point of intersection for all the curves, owing to experimental inaccuracy. However, it is always possible to find the value of r for which the variation of k_0^*

is smallest. In the following treatment of the experimental results we shall see examples of both methods of computation here described. Owing to the mathematical form of expression 13, a small error in x and t will cause rather a great inaccuracy in k_0^* and h_0^* (see figure 1 and table 3).

If equation 13 is satisfied for all the experimental pairs of x and t by $r = \frac{1}{2}$ and a certain value of k_0^*, say $k_0^* = y$, it will, as seen from equations 14 and 16, also be satisfied by $r = \infty$ and $k_0^* = \frac{y}{2}$. If $(y, \frac{1}{2})$ is the common point for all the k_0^*,r-curves, they will all approach the straight line $k_0^* = \frac{y}{2}$ asymptotically when $r \rightarrow \infty$. Consequently, in this case it is impossible to decide from the experiments whether $r = \frac{1}{2}$ and $k_0^* = y$, or $r = \infty$ and $k_0^* = \frac{y}{2}$. It is seen from figure 1, that if the common point of intersection for all the k_0^*,r-curves falls in the interval $\frac{1}{2} < r < \infty$, each curve will cut each of the other curves in another point in this interval, but the new points of intersection are not common for all the curves. It is useful to remember this when computing the constants. Otherwise there is danger of finding a false solution, especially when using the first of the two methods.

EXPERIMENTAL

Materials

Kahlbaum's best preparation of acetoacetic ester was purified in one of the following two ways. (1) With sodium bisulfite as suggested by Elion (3). The ester was dissolved in a little less than the calculated amount of saturated sodium bisulfite solution. An impurity which does not combine with bisulfite was removed by extraction with ether. The ester was again liberated by addition of the calculated amount of potassium carbonate and extraction with ether. After drying with anhydrous sodium sulfate the ether was distilled from the ester. Finally, the ester was distilled several times in vacuo. (2) Through the copper compound. This compound was made by shaking an ethereal solution of acetoacetic ester with an aqueous solution of copper acetate (Wislicenus (4)). The copper compound was three times recrystallized from benzene and then decomposed with hydrochloric acid. The ester was extracted with ether and, after drying with anhydrous sodium sulfate, was twice distilled in vacuo.

Samples of the two preparations were left for fifteen to twenty hours with an excess of sodium hydroxide solution and afterwards titrated with hydrochloric acid. It was found that one equivalent of base hydrolyzed 130.0 g. of the first and 130.1 g. of the second preparation. The calculated molecular weight is 130.08.

The bromine water was prepared from Kahlbaum's bromine "for analysis."

Experimental procedure

A beaker with acetoacetic ester solution (usually 175 cc.), containing in most of the experiments varying amounts of hydrochloric acid or neutral salts, was placed in a thermostat at 24.97°C. or 17.94°C. or in an ice-water mixture. The solution was stirred mechanically. Its temperature could be read off on a thermometer. Bromine water (usually 25 cc. of 0.15 N) was brought to the same temperature. The reaction was started by mixing the two solutions. It was stopped after some time (t minutes) by adding an excess of allyl alcohol dissolved in water. This reacts instantaneously with the remaining free bromine. The time was measured by means of a stop-watch which had been compared with an accurate pendulum clock. The corrections never exceeded 0.2 second. Immediately after the reaction was stopped, an excess of solid potassium iodide (1 to 2 g.) and a little dilute hydrochloric acid was added. Iodine equivalent to the bromine used by the reaction is liberated

$$CH_3COCHBrCOOC_2H_5 + 2I^- + H^+ \rightarrow CH_3COCH_2COOC_2H_5 + I_2 + Br^-$$

and

$$CH_3COCBr_2COOC_2H_5 + 4I^- + 2H^+ \rightarrow CH_3COCH_2COOC_2H_5 + 2I_2 + 2Br^-$$

The iodine was titrated with 0.05 N thiosulfate and starch solution. The liberation of iodine does not take place instantaneously. The thiosulfate was added in small portions, and the titration was considered as finished when the solution stayed colorless for five minutes after addition of one drop of 0.05 N thiosulfate. Usually the titration took fifteen to twenty minutes. Dissolved oxygen and small amounts of impurity in the chemicals used may oxidize some iodide during the titration. In order to correct for this error a blank experiment without acetoacetic ester was done for each series of experiments. It used always less than 0.10 cc. of thiosulfate. In the experiments at 0°C. the solution was slowly heated to room temperature during the titration. Both the bromination and the analysis were carried out in diffused daylight or artificial light. Neither the bromopropyl alcohol formed by the reaction between bromine and allyl alcohol, nor the excess of allyl alcohol interfered during the analysis. The former does not liberate iodine from iodide; the latter reacts too slowly with iodine. Fortunately it is unnecessary to know the exact concentration of bromine during the reaction, the velocity being independent of the amount of bromine.

It was found to be important to add the potassium iodide immediately after the bromination was stopped. If the solution was left for some time before analysis, too little thiosulfate was used, and the last part of the liberation of iodine was much slower than usually. In this case it was noticed that the solution had a sharp smell. Probably the bromo- or dibromo-acetoacetic ester is slowly transformed into compounds which react more slowly with iodide. This may also explain why the results of the analysis are lower than expected in experiments where the bromine has reacted for a very long time. With extremely long times of reaction the bromine found by the analysis even decreased when the time of bromination was increased. In such experiments the solution was cloudy after the bromination. This error adds to the difficulty in computing the velocity constants k_0^* and h_0^* from the experimental results.

In a great number of experiments it was shown that the velocity is independent of the bromine concentration. This is seen most distinctly from some experiments carried out in another way. To the solution of acetoacetic ester was added insufficient bromine water, and the moment when the reaction ceased because all the bromine had reacted was determined electrometrically. Into the beaker dipped a platinum electrode, and the solution was connected by means of an agar-agar bridge with a glass containing a solution of iodine and potassium iodide into which dipped another platinum electrode. The electrodes were connected with a galvanometer through a high resistance. As long as bromine was present the galvanometer gave a slowly decreasing deflection. When the last trace of bromine disappeared the zero was quickly passed, and the galvanometer gave a considerable deflection in the opposite direction. The time from the mixing of the solutions until the disappearance of the bromine was measured. Potassium iodide was added to the solution, and the analysis was carried out in the usual way. The time of reaction was varied by adding varying amounts of bromine water in the different experiments. Experiments carried out in this way gave exactly the same results as experiments with an excess of bromine and interruption by means of allyl alcohol. This shows conclusively that the velocity is independent of the concentration of bromine. Consequently, the reaction by which bromine is taken up is very rapid compared with the reaction which determines the actual velocity of the complete process. The allyl alcohol method, being the simplest and most accurate, was used for all the experiments whose numerical results are given below.

The results of a series of experiments on the bromination of acetoacetic ester in water at 17.94°C. are given in table 1. The initial concentration of bromine was 0.025 M, and that of the ester 0.005062 M except in experiments marked thus (†), where it was 0.01736 M. By extrapolation to $t = 0$ it was found that $\epsilon = 0.0034$. By plotting $\log \frac{c - \frac{x}{4}}{c}$ against t, the values $k_0^* = 0.01802$ and $h_0^* = 0.206$ were found. In order to test the agreement with formula 13, $\frac{x}{4}$ was calculated from the formula, using the

TABLE 1

Bromination of acetoacetic ester in water at 17.94°C.

$c = 5.062 \times 10^{-3}$. In the experiments marked †, $c = 17.36 \times 10^{-3}$. $\epsilon = 0.0034$. $k_0^* = 0.01802$. $h_0^* = 0.206$.

t	$\frac{x}{4} \times 10^3$	$\frac{c - \frac{x}{4}}{c}$	$A\,10^{-k_0^* t}$	$\left(A - 1 + \frac{\epsilon}{2}\right) 10^{-h_0^* t}$	$\frac{x}{4} \times 10^3$ (calcd.)	$\delta \times 10^6$
†0.083	0.063	0.9964	1.0406	0.0440	0.059	+4
†0.258	0.132	0.9924	1.0328	0.0405	0.134	−2
†0.500	0.240	0.9862	1.0226	0.0363	0.238	+2
†1.00	0.470	0.9729	1.0014	0.0286	0.473	−3
1.00	0.140	0.9725	1.0014	0.0286	0.138	+2
†2.00	0.993	0.9428	0.9607	0.0177	0.990	+3
2.00	0.286	0.9438	0.9607	0.0177	0.288	−2
†3.00	1.540	0.9113	0.9222	0.0110	1.542	−2
3.00	0.454	0.9105	0.9222	0.0110	0.450	+4
4.00	0.618	0.8782	0.8847	0.0069	0.619	−1
5.00	0.786	0.8449	0.8488	0.0043	0.787	−1
6.00	0.943	0.8140	0.8141	0.0027	0.954	−11
7.00	1.118	0.7793	0.7809	0.0017	1.117	+1
8.00	1.277	0.7475	0.7490	0.0011	1.276	+1
10.00	1.575	0.6891	0.6894	0.0004	1.574	+1
12.00	1.851	0.6345	0.6349	0.0002	1.847	+4
15.00	2.226	0.5604	0.5604	0.0000	2.225	+1
18.00	2.552	0.4960	0.4948	0.0000	2.557	−5
24.00	3.090	0.3897	0.3857	0.0000	3.109	(−19)

$\delta_m = 3.6 \times 10^{-6}$

TABLE 2

Bromination of acetoacetic ester in 0.050 M potassium bromide at 17.94°C.

c = 5.056. In experiments marked †, $c = 6.275 \times 10^{-3}$. $\epsilon = 0.0040$. $k_0^* = 0.01780$. $h_0^* = 0.216$.

t	$\frac{x}{4} \times 10^3$	$\frac{c - \frac{x}{4}}{c}$	$\frac{x}{4} \times 10^3$ (calcd.)	$\delta \times 10^6$
0.053	0.016	0.9968	0.016	0
0.080	0.019	0.9963	0.019	0
1.00	0.139	0.9725	0.136	+3
2.00	0.291	0.9425	0.288	+3
4.00	0.619	0.8776	0.619	0
6.00	0.948	0.8125	0.952	−4
†8.00	1.570	0.7499	1.575	−5
10.00	1.561	0.6912	1.564	−3
†12.00	2.283	0.6362	2.281	+2
†14.00	2.600	0.5857	2.595	+5
16.00	2.324	0.5404	2.324	0

$\delta_m = 3.1 \times 10^{-6}$

values of ϵ, k_0^* and h_0^* here computed. The last column of the table gives the difference δ between the observed and calculated values of $\frac{x}{4}$. The agreement is good, except when $\frac{c - \frac{x}{4}}{c} < \frac{1}{4}$. Here the observed values are smaller than calculated from the formula. This discrepancy was mentioned above. In order to express how well the course of the reaction agrees with the formula, we calculate $\delta_m = \frac{\sqrt{\Sigma\delta^2}}{n-1}$, where n is the number of experiments. If we disregard the last experiment, we get $\delta_m = 3.6 \times 10^{-6}$.

Table 2 gives the results of a series of experiments in 0.050 M potassium bromide at 17.94°C. treated in the same way. It is seen that bromide ions have only a slight effect on the velocity.

TABLE 3

Calculation of k_0^* from formula 13 for different values of r

The same series of experiments as in table 2

t	$k_0^* \times 10^4$						
	$r = 0.5$	$r = 2$	$r = 6$	$r = 10$	$r = 12$	$r = 15$	$r = \infty$
1.00	224	216	197	186	181	173	112
2.00	249	230	202	185	179	172	124
4.00	276	243	202	184	179	171	138
6.00	298	245	200	183	179	172	149
8.00	310	245	198	182	178	173	155
10.00	320	243	196	182	179	174	160
12.00	326	241	193	181	179	175	163
14.00	330	238	193	181	179	176	165
16.00	332	235	191	181	179	176	166

The experimental results of this series have also been computed in the second and more difficult way described above. As seen from table 3 the variation of the calculated k_0^* values is smallest when $r = 12$, giving as mean value $k_0^* = 0.0179$ and $h_0^* = 0.21$ in agreement with the values found in table 2. In figure 1 is given a graph of the computation. For simplicity only four experiments are represented. It is seen that each curve cuts each of the other curves in one point in addition to the point of intersection common to them all. As seen from the table and diagram, we may vary r considerably without impairing the constancy of k_0^* appreciably. Therefore, the constants k_0^* and h_0^* are not determined as accurately as might be expected from the good agreement between the observed and calculated values of $\frac{x}{4}$.

Table 4 contains a summary of twenty series of experiments on the bromination in aqueous solutions of hydrochloric acid, sodium chloride, and potassium chloride, all at 18°C., and, finally, of potassium bromide at 0°, 18° and 25°C. The salts were Kahlbaum's or Merck's "for analysis." The initial concentration of acetoacetic ester was usually about 5×10^{-3} M, but in a few experiments three to four times as great. All concentrations are given in moles per liter. In our computation of the constants we have disregarded those experiments with long times of reaction where the fall in x mentioned above made its appearance. All the experiments in the first half of the reaction $\left(\frac{c - \frac{x}{4}}{c} > \frac{1}{2}\right)$ have been used. The number, n, of experiments used is given in table 4 for each series. The agreement with formula 13 is always good. The mean value of δ_m for the twenty series of experiments is 3.0×10^{-6}. The volume during the reaction being 200

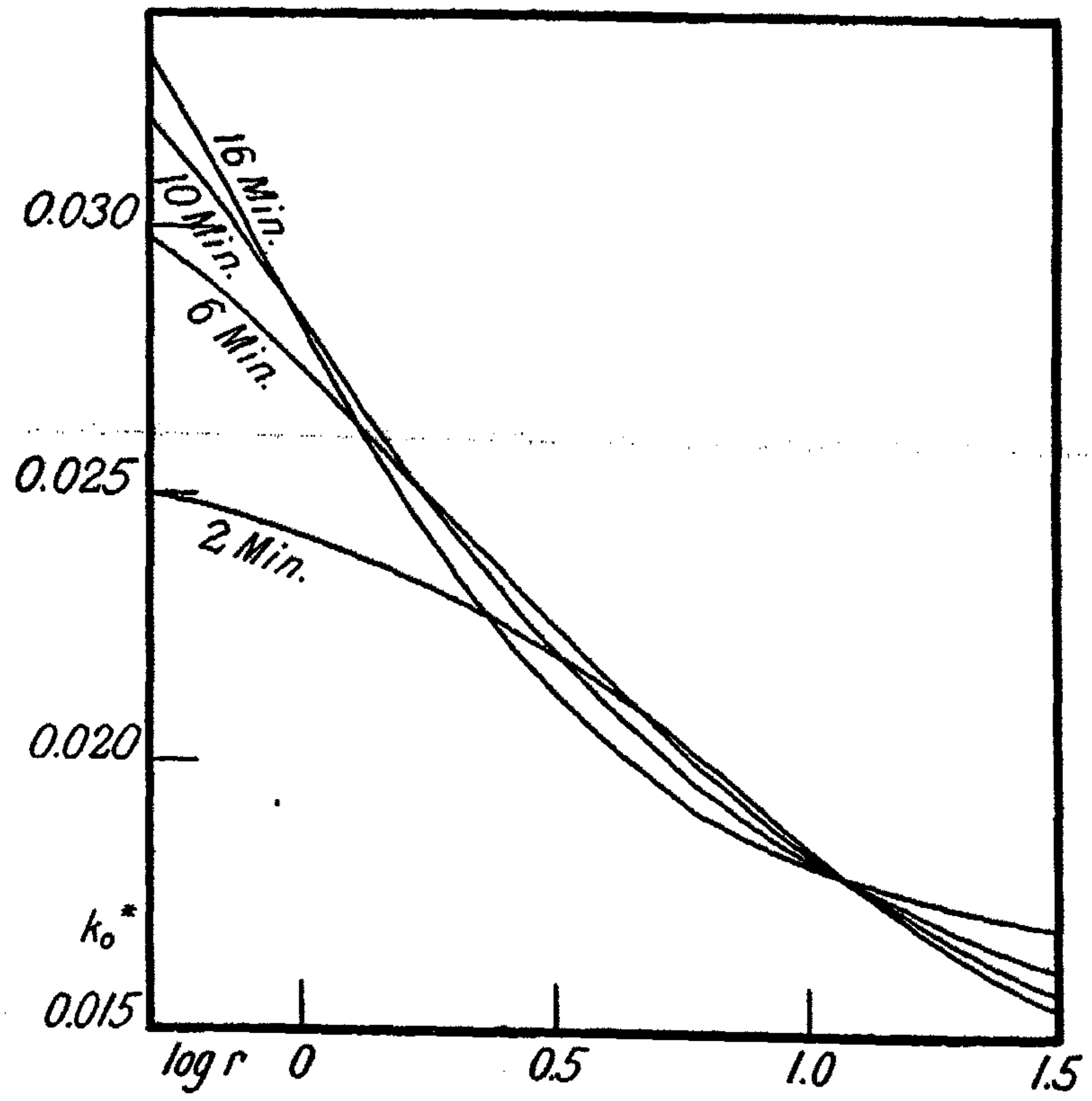

FIG. 1. COMPUTATION OF k_0^* AND r OF THE EXPERIMENTS IN TABLES 2 AND 3

cc., $\delta = 3.0 \times 10^{-6}$ corresponds to 0.05 cc. of 0.05 *N* thiosulfate. In all the solutions the reaction may be expressed by formula 13 with an accuracy corresponding to the experimental error. The total non-systematical part of the experimental error thus corresponds to an average error of 0.05 cc. on the titration.

In figure 2 the velocity constants k_0^* of the enolization of acetoacetic ester at 18°C. in solutions of hydrochloric acid, sodium chloride, potassium chloride, and potassium bromide are plotted against the concentration *M* of the acid or salt. The decrease in k_0^* caused by the three salts is approximately proportional to the concentration. However, this primary salt effect is not great, only a few per cent in 0.1 *M* solution. The effect on the enolization of monobromoacetoacetic ester is nearly the same. Thus *r* is almost constant for all the solutions, as seen from table 4.

TABLE 4

Bromination of acetoacetic ester in water and aqueous solutions of hydrochloric acid, sodium chloride, potassium chloride, and potassium bromide

t *degrees C.*	SOLVENT	n	ϵ	k_0^*	h_0^*	$\delta_m \times 10^6$	r
17.94	Water	18	0.0034	0.01802	0.206	3.6	11.4
	HCl 0.0424 *M*	16	0.0040	0.01843	0.187	2.6	10.1
	HCl 0.0986 *M*	15	0.0038	0.01869	0.187	4.2	10.0
	HCl 0.1970 *M*	11	0.0038	0.01905	0.191	2.0	10.0
	HCl 0.370 *M*	10	0.0042	0.01955	0.196	2.4	10.0
	NaCl 0.100 *M*	10	0.0037	0.01785	0.215	4.0	12.0
	NaCl 0.300 *M*	10	0.0037	0.01729	0.195	2.1	11.3
	NaCl 0.400 *M*	10	0.0037	0.01704	0.190	2.2	11.2
	NaCl 0.500 *M*	10	0.0037	0.01667	0.186	2.1	11.2
	NaCl 0.600 *M*	10	0.0037	0.01626	0.180	2.4	11.1
	NaCl 0.700 *M*	12	0.0036	0.01592	0.178	2.4	11.2
	NaCl 0.800 *M*	10	0.0036	0.01557	0.174	2.3	11.2
	NaCl 1.000 *M*	9	0.0036	0.01481	0.168	2.6	11.3
	NaCl 2.000 *M*	7	0.0018	0.01133	0.147	3.1	13.0
	KCl 0.596 *M*	10	0.0040	0.01563	0.186	1.2	11.9
	KCl 0.894 *M*	10	0.0036	0.01443	0.174	4.3	12.0
	KCl 1.192 *M*	12	0.0040	0.01337	0.150	3.9	11.2
0.03	KBr 0.050 *M*	12	0.0035	0.00353	0.0425	5.6	12.0
17.94	KBr 0.050 *M*	11	0.0040	0.01780	0.216	3.1	12.1
24.97	KBr 0.050 *M*	13	0.0045	0.03120	0.384	3.5	12.3

Addition of hydrochloric acid causes an increase of k_0^* of the same order of magnitude as the decrease caused by the salts. The effect is so small that it is hardly possible to decide whether it is caused only by a primary salt effect of the hydrochloric acid, or whether a hydrogen ion catalysis has a share in it. If there is any acid catalysis it is very slight. Thus the increase in 0.1 M hydrochloric acid is only 4 per cent. For comparison we may mention that the basic catalysis, which we shall deal with in the next part of this paper, is very pronounced. Thus the weak base, the acetate ion, in the concentration 0.1 M causes the velocity to rise to about forty times its value in water.

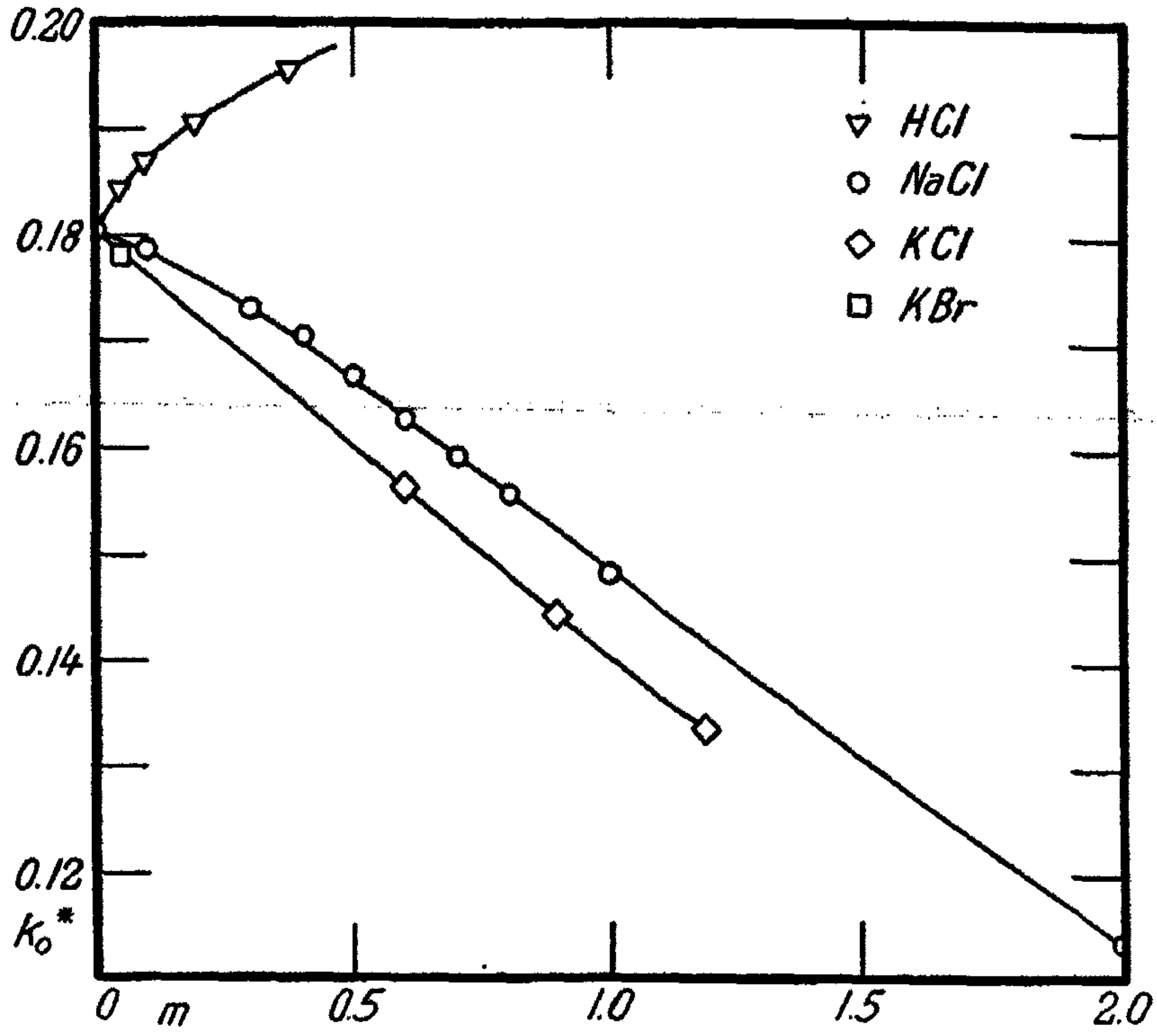

Fig. 2. Bromination of Acetoacetic Ester in Solutions of Hydrochloric Acid and Natural Salts

According to the scheme in equations 1a to 1d small amounts of hydrogen and bromide ions are formed by the reaction. We have seen that the effect of these ions is so small that their formation can have no influence on the velocity.

It is of interest to compare these results with some earlier measurements on the velocity of isomerization of acetoacetic ester carried out by Meyer (5). In one case he dissolves acetoacetic ester, containing 7 per cent of enol, in water at 0°C. and follows the decrease in enol by titration with bromine water at different times (1/6 to 1 minute after dissolving the ester). The reaction being balanced, the unimolecular constant calculated in the usual way is the sum of the constants for the ketonization and for the enolization $k_{\text{ket.}} + k_{\text{enol}}$. Meyer finds at 0°C. the constant 2.4, from which he calculates, using $k_{\text{enol}}/k_{\text{ket.}} = \epsilon/1 - \epsilon = 0.004$, $k_{\text{ket.}} = 2.4$ and $k_{\text{enol}} = 0.010$, that is, $k_{\text{enol}} = 0.0043$. If, instead of Meyer's value of ϵ, we use the value found in this paper at 0°C., $\epsilon = 0.0035$, we get $k_{\text{enol}} = 0.0036$, in good agreement with the value 0.00357 found here (calculated from our value in 0.05 *M* potassium bromide, assuming that the relative decrease by addition of 0.05 *M* potassium bromide is the same at 0°C. as at 18°C.).

In other experiments Meyer added varying amounts of bromine water to old solutions of acetoacetic ester at 0°C. (in one series at 10°C.) and determined the time when the color of the bromine had just disappeared. However, in his calculation of the velocity constant Meyer takes into account only the enolization of the acetoacetic ester, not being aware that it is followed by the much quicker enolization of the monobromoacetoacetic ester. Here his results are recalculated, taking into regard both enolizations. For comparison values of k_0^* from the experiments in this paper are given in the last column.

	k_0^* (Meyer recalcd.)	k_0^* (Pedersen)
Water 0°C.	0.0031	0.00357
Water 10°C.	0.0088	0.0090
0.1 *N* HCl 0°C.	0.0038	0.00371

While Meyer's experiments in water at 10°C. and in hydrochloric acid at 0°C. agree well with those in this paper, there is a fairly great discrepancy in water at 0°C. From the considerable rise in k_0^* when going from water to 0.1 *N* hydrochloric acid (Meyer actually found by his method of computation an increase of 40 per cent), he concludes that hydrogen ions have catalytic effect. This result is not confirmed by the present investigation.

SUMMARY

In the bromination of acetoacetic ethyl ester four consecutive reactions could be distinguished. (1) The acetoacetic ester is enolized, and (2) brominated to the keto form of α-monobromoacetoacetic ester; (3) this is enolized, and (4) brominated to α, α-dibromoacetoacetic ester. Only (1) and (3) take place with measurable velocity. The unimolecular velocity constants of the enolization of acetoacetic and of monobromoacetoacetic ester in water and aqueous solutions of hydrochloric acid, sodium chloride, potassium chloride, and potassium bromide have been computed from the experiments. The reaction is not catalyzed by hydrogen ions to any perceptible degree.

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THE INFLUENCE OF SMALL AMOUNTS OF DISSOLVED SILICATES ON THE CONDUCTANCE OF CONDUCTIVITY WATER AND VERY DILUTE SOLUTIONS OF ELECTROLYTES

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INTRODUCTION

The magnitude and sign of the solvent correction to be made in conductivity data is sometimes very uncertain, and its application has been the subject of much discussion and controversy in the past few years. This arises mainly from uncertainties as to the impurities present in conductivity water and their reaction with the electrolyte in solution. Kendall's (1) "carbonic acid correction" has not been generally accepted, partly because of the maximum observed at high dilutions in the data for strong acids even after the correction had been made, and partly because some authors have found disturbing factors greater than the carbon dioxide present. Washburn (2) suggests that this "abnormal behavior" is probably due to the presence of some basic or saline impurities, while Whetham and Paine (3) attribute it to a salt, probably ammonium carbonate.

Though it is conceded that carbon dioxide is generally the major impurity, Wynne-Jones (4) has shown a deviation between the calculated and theoretical curves and suggests that solution of silica from the cell walls might cause the variation. Kraus and Parker in their work on iodic acid with concentrations as low as .00005 *N*, using very pure water and cells of quartz, Pyrex, and soda-lime glass have shown that the nature of the cell is of greater importance than the initial conductivity of the water or the carbon dioxide content.

The extent of the solubility or decomposition of glass under the conditions ordinarily met with in conductance work has not as yet been studied very thoroughly. Such measurements would be difficult to make and reproduce, because there are so many factors influencing the decomposition and rate of solution. Glasses also vary much in their physical and chemical constitution, even those of the same brand. Glass in contact with moist air and carbon dioxide is continually being acted upon, giving products which are easily soluble in water. Thus solutions put in such a container, which has not been well leached just before use, will be affected abnormally at first. This phenomenon is easily noticeable by pouring a very dilute solution of hydrochloric acid into a bottle which has been standing open to air. The reduction in conductance at first is comparatively large, changing only gradually thereafter.

Forester's (5) and Walker's (6) work on the solubility of glass under laboratory conditions shows that it is by no means negligible, and that both alkali and silica are taken into solution, probably in the form of a sodium silicate. The nature and behavior of the silicates of sodium in solution has been studied quite thoroughly by Haag (7) and by Harman (8). From their work it has been concluded that the only sodium silicates existing in solution as such are the metasilicate, Na_2SiO_3, and the disilicate, $NaHSiO_3$; that the hydrolysis of Na_2SiO_3 gives rise to $HSiO_3^-$ ions, which do not separate out colloidally; that only ratios larger than $Na_2O:SiO_2 = 1:2$ give appreciable amounts of colloidal silicic acid. In addition, Harman has shown that in dilute solutions of any ratio, practically all the silica exists in the crystalloidal state. Under the term "crystalloidal silica," he classifies definite silicate and bisilicate ions, aggregates of ions carrying an electric charge with or without colloidal silica, i.e., ionic micelles and crystalloidal silicic acid or hydrated silica.

The present investigation is an attempt to show the effect of small amounts of sodium silicates, such as are dissolved from glasses, on very dilute solutions of electrolytes and on conductivity water. Although there is no definite proof that the material dissolved or decomposed from the glass is in the form of silicates of sodium, it is shown from equilibrium relations between the crystalloidal silica and alkali that effectively it is in that form. Further, the solution of glass and change in the nature of impurities in conductivity water with collection and storage in Pyrex and soft glass containers will be demonstrated.

EXPERIMENTAL

The conductivity apparatus was one arranged and set up by Alonzo W. Martin.[1] A telephone head-set tuned to a 1000 cycle E.M.F. from a Vreeland oscillator was used as a detector. To increase its sensitiveness a one-stage audio tube amplifier, as suggested by Hall and Adams (9) was placed in series with the telephone. A Kohlrausch drum-wound slidewire bridge divided in one thousand divisions was calibrated for use by the method of Stronhal and Barus. For the resistance, two calibrated Curtiss coils of capacities 10,000 ohms and 100,000 ohms were used. Adjustable air condensers cut out all capacitance and eddy currents, thereby increasing the sensitiveness and clearness of the minimum point. The whole apparatus was well grounded with a grounding arrangement similar to that suggested

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[1] The writer is indebted to Professor Martin for the use of the apparatus.

by Wagner (10). Measurements were made in a thermostat regulated to 25°C. The dip-type conductance cell with bright platinum electrodes was used so it could be dipped into the solutions through the neck of a well leached liter Pyrex flask. The cell constant was obtained by inter-comparison on a 0.001 N solution of potassium chloride, which value checked very closely with that obtained by using 0.0014695 mhos for the specific conductance of the potassium chloride (11). Its value was taken as 0.081402.

Stock solutions of hydrochloric acid, potassium chloride, and sodium hydroxide were carefully made up from the C.P. materials. These were measured out in standard calibrated pipettes and diluted to the desired concentration. One liter of the solution was transferred to the conductance arrangement; the whole was well but gently stirred after the addition of each increasing amount of 0.00046 N sodium silicate; the electrodes were raised and lowered several times in the solution and a short time was allowed for equilibrium to become closely established, after which all readings were immediately taken. Care had to be used throughout to prevent as far as possible the adsorption of carbon dioxide from the air and to prevent any vigorous motion, since it increases the amount of glass dissolved from the apparatus. Extreme accuracy was not aimed at, since at such high dilutions accurate values of conductance would be of little value, because the exact nature of all the impurities in the water is not known, and the exact behavior of electrolytes at these extreme dilutions is not fully understood. The sodium silicate used was made up from Baker's 40 per cent solution having, according to their analysis, a $Na_2O:SiO_2$ ratio of 1 : 3.22. The normality with respect to sodium was 0.00046.

The conductivity water was obtained from a specially constructed Kraus type still charged with alkali-permanganate. Water ranging in conductance from 0.4×10^{-6} to 1.4×10^{-6} was prepared, and the effect of sodium silicate on conductance of water with different initial conductivities noted. The results are given in graphs (figure 1) rather than in tables, since the nature of the changes is more easily seen and compared. The results showing the effect of small amounts of sodium silicate on the conductance of very dilute solutions of hydrochloric acid, sodium hydroxide, and potassium chloride are given in figures 2, 3, and 4, respectively. In order to demonstrate the rate and extent to which silicates dissolve from Pyrex and soft glass containers, water was left standing in 10-liter bottles, both sealed and open. At various times 1-liter samples were drawn and conductometric titrations run with sodium silicate, as above, to show how much carbon dioxide had been removed by action of dissolved silicates. Many such runs under varying conditions were made, and some representative results are given in figures 5 and 6.

DISCUSSION

From the curves of figure 1, it is seen that the manner in which the conductance changes with increasing amounts of sodium silicate varies widely with the initial conductivity of the water. The higher the initial conductivity, the greater is the total lowering of the conductance and the more sodium silicate required to cause the maximum depression. A comparison of these curves with those of hydrochloric acid (figure 2) and sodium hydroxide (figure 3) shows quite definitely that the main impurity in the water is acidic in nature and without doubt is carbonic acid. The conductance of water of lower conductivity than 0.5×10^{-6} is seen to rise continuously, thus showing that either there is no carbon dioxide present below this

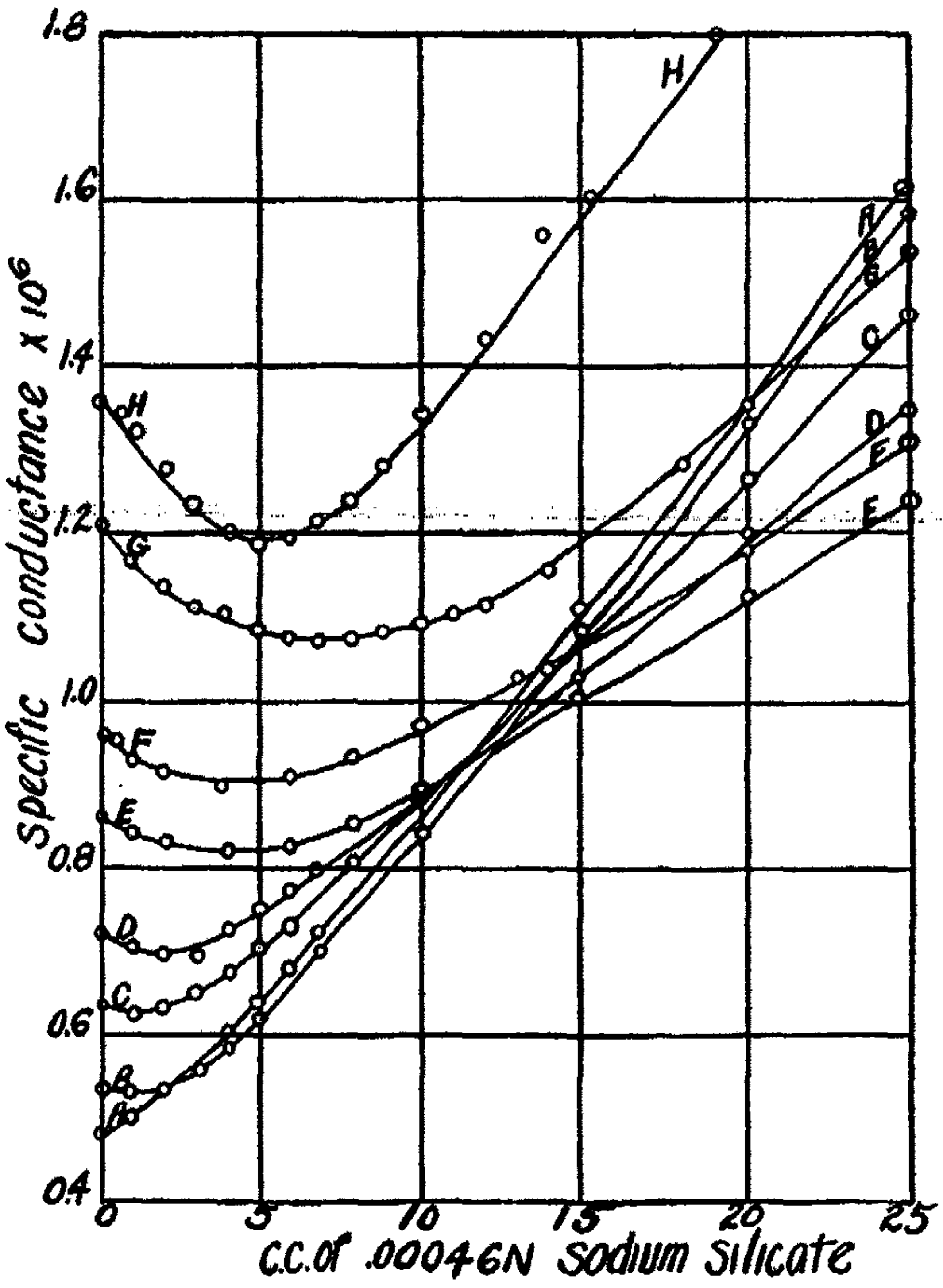

Fig. 1. Effect of Sodium Silicate on the Conductance of Conductivity Water of Varying Initial Specific Conductivities

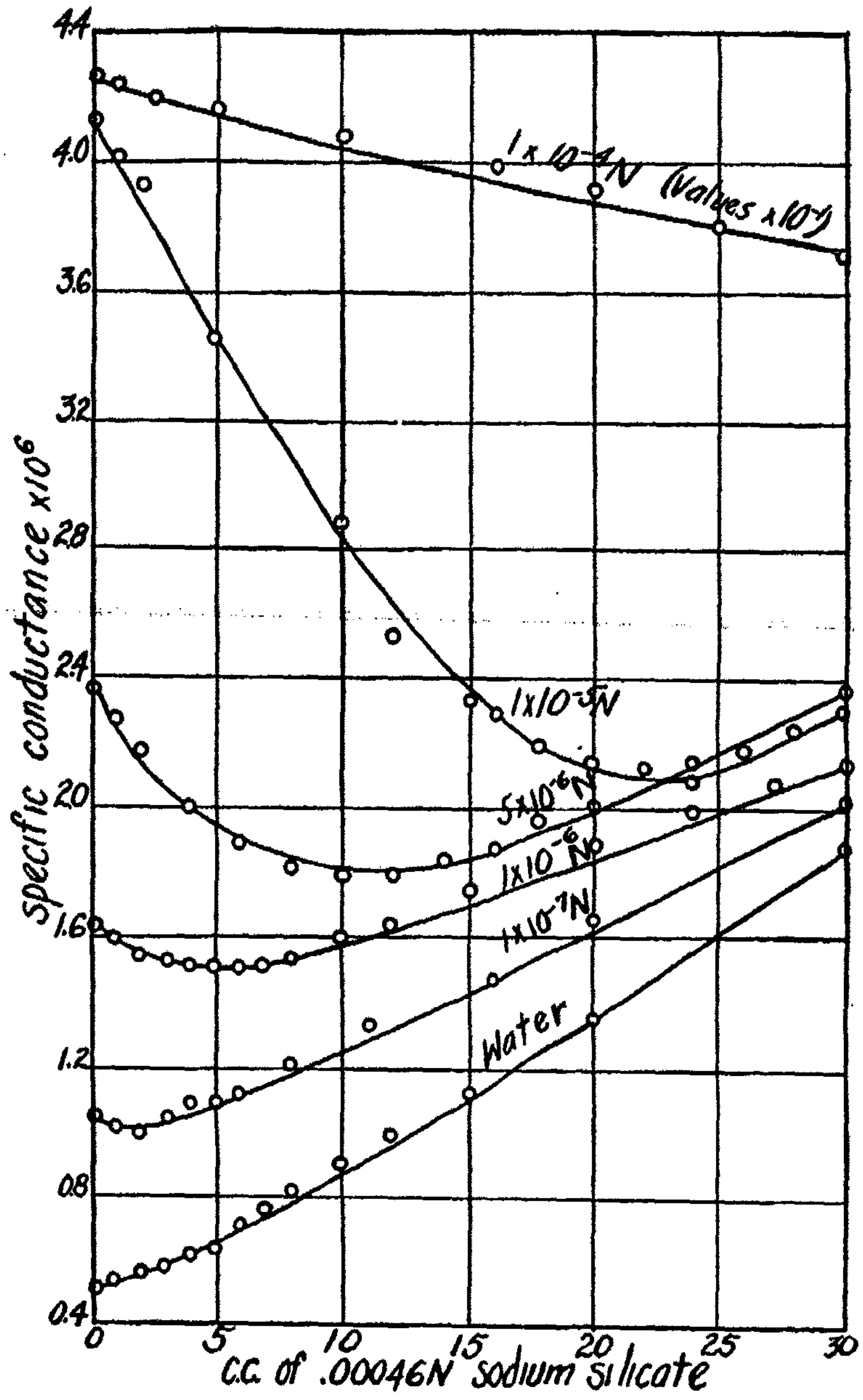

FIG. 2. EFFECT OF SODIUM SILICATE ON CONDUCTANCE OF HYDROCHLORIC ACID SOLUTIONS

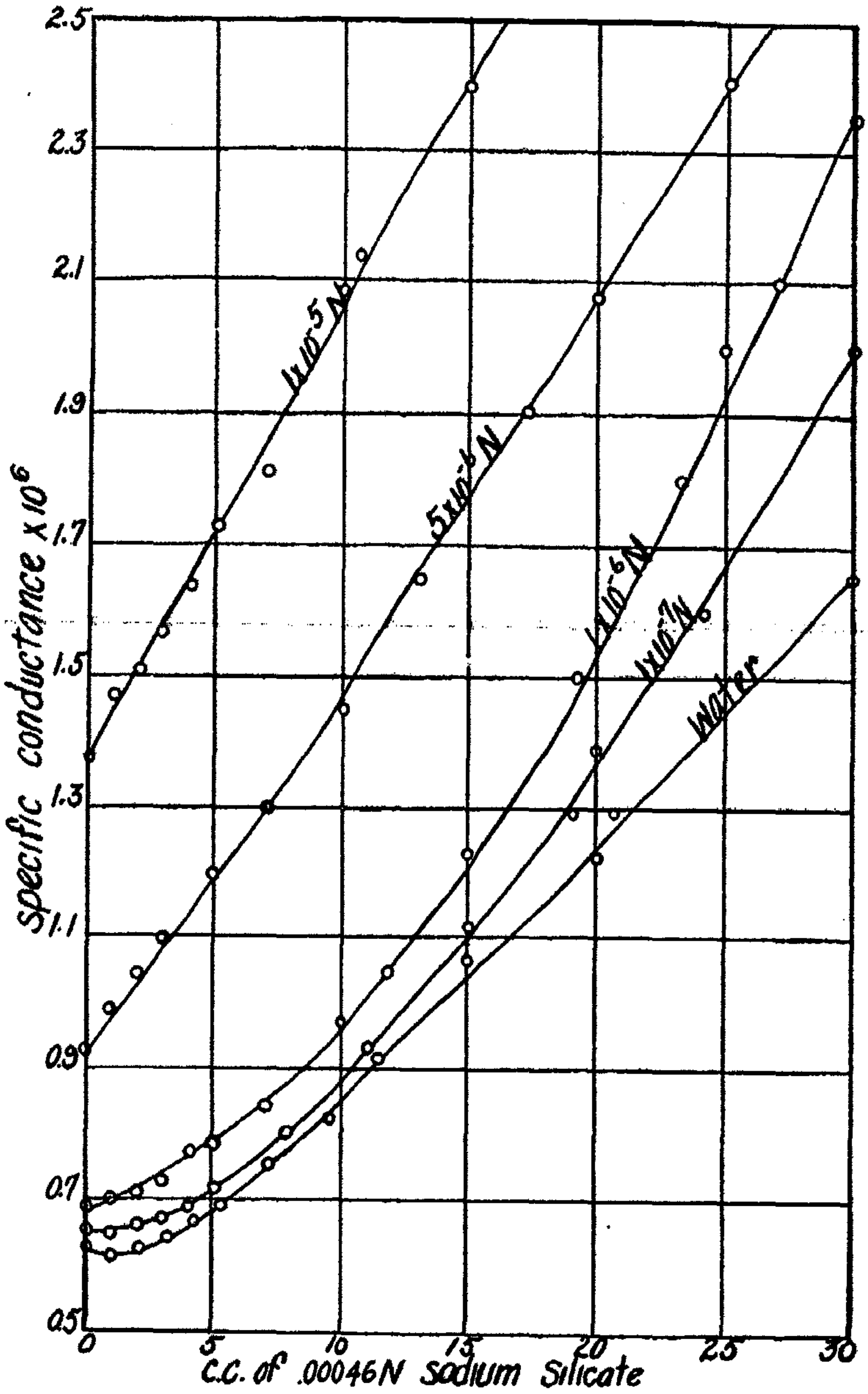

FIG. 3. EFFECT OF SODIUM SILICATE ON CONDUCTANCE OF SODIUM HYDROXIDE SOLUTIONS

value, or that all the carbon dioxide has been removed by reaction with sodium silicate dissolved from the Pyrex container while the water was being collected. The latter is probably the case. It is seen from these curves that a "carbonic acid" solvent correction cannot be applied to water below

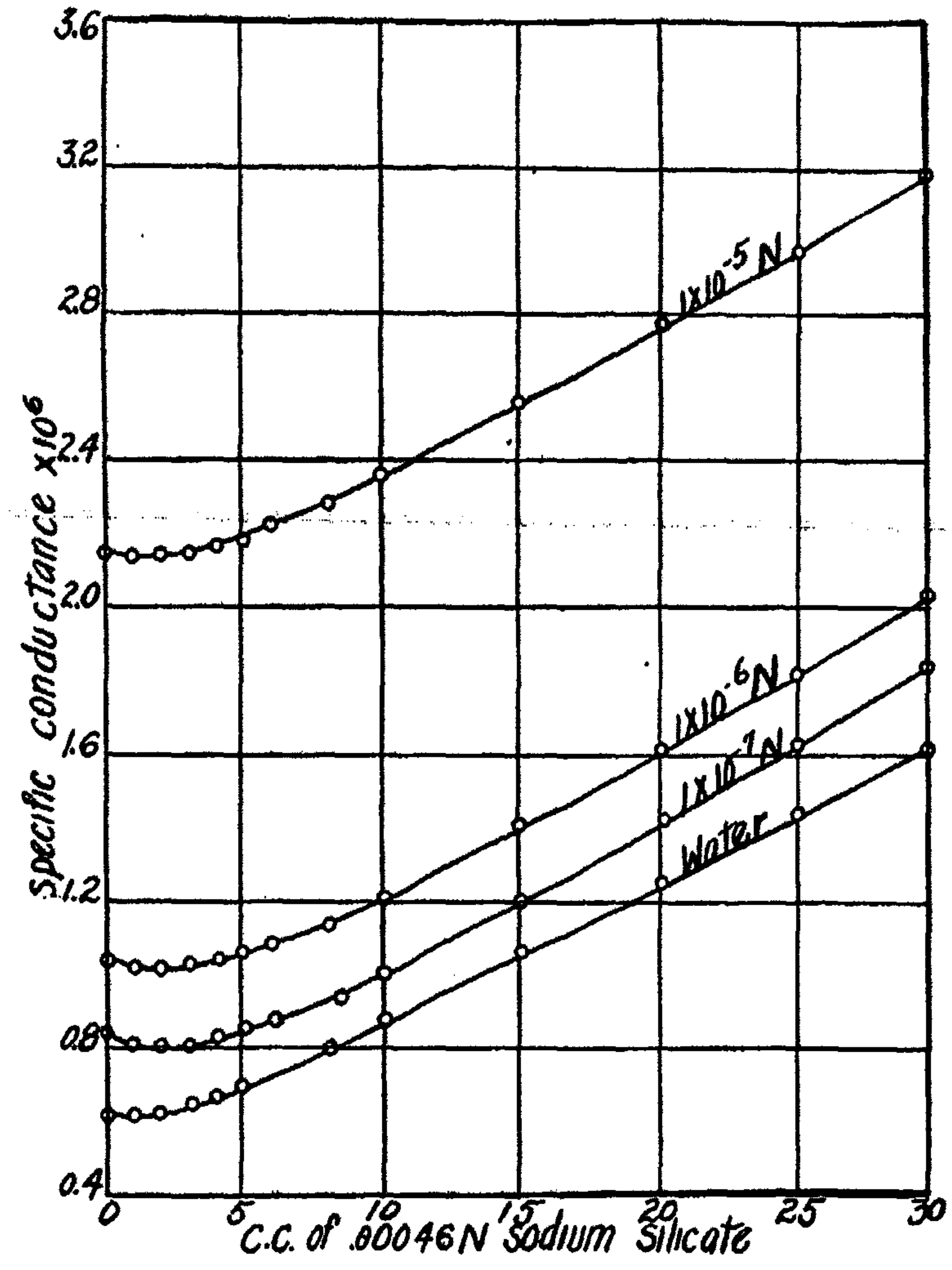

FIG. 4. EFFECT OF SODIUM SILICATE ON CONDUCTANCE OF POTASSIUM CHLORIDE SOLUTIONS

0.5×10^{-6} if it has been collected hot in Pyrex containers. The correction will rather be one for the "solution of glass," which involves a consideration of the products formed in the reaction of carbonic acid with silicates of sodium. For water of higher initial conductivity it is seen that the

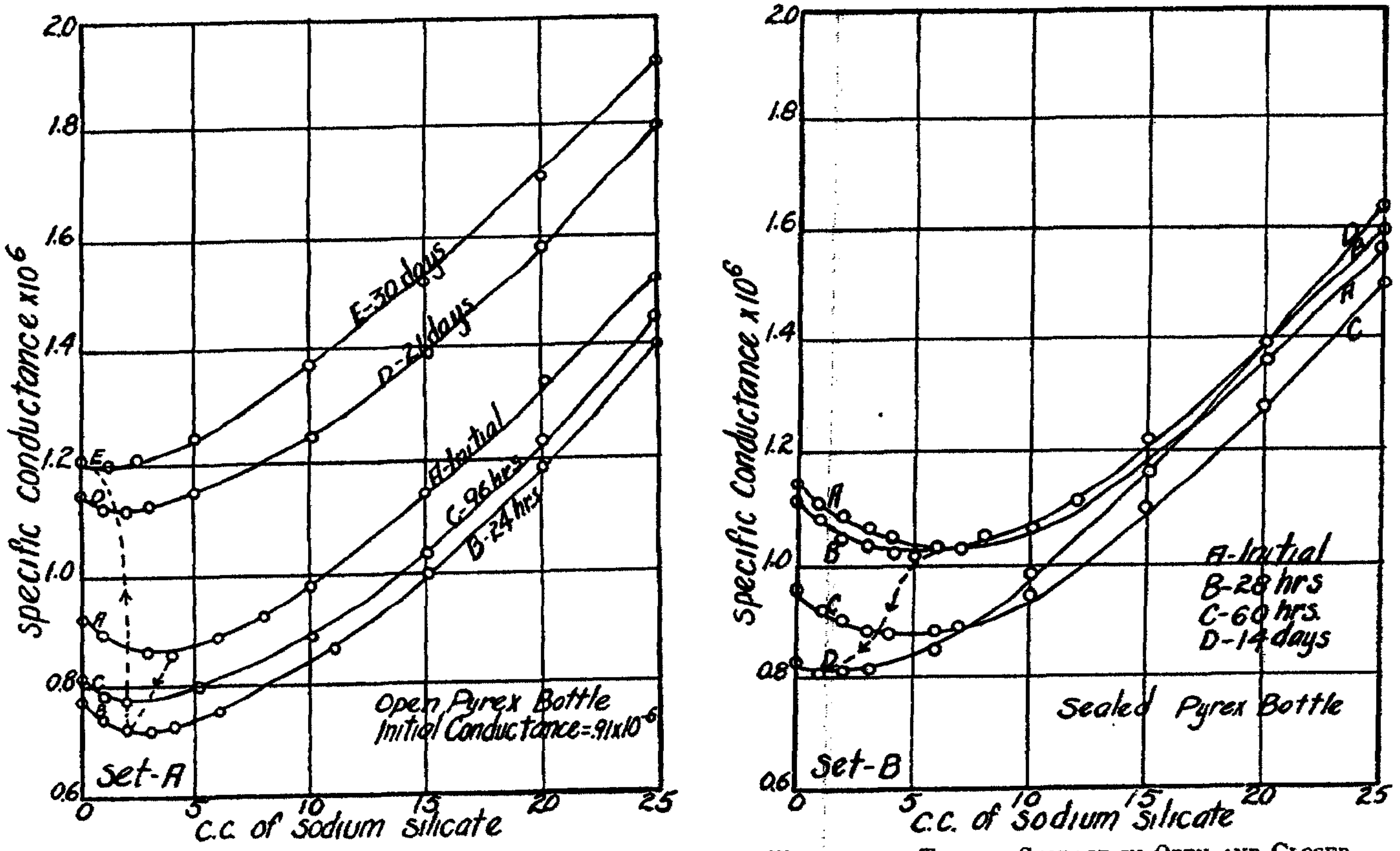

Fig. 5. Change of Carbon Dioxide Content of Conductivity Water with Time of Storage in Open and Closed Pyrex Bottles at 25°C.

correction will have to take into account both the carbon dioxide and the dissolved glass.

After the water has been collected, the relative amounts of carbon dioxide and dissolved silicates will vary with the time of storage. This is clearly shown by the curves of figures 5 and 6. The conductance of water in equilibrium with carbon dioxide of the air is 0.8×10^{-6}. The conductance of the water should tend toward this value, and the amount of sodium silicate required for maximum depression should be approximately 5 cc. (see figure 1) if no foreign substances interfered. From the curves it can be seen that the carbon dioxide is continually being removed, while the amount of dissolved glass increases. Thus with a Pyrex bottle, practically all the carbon dioxide has reacted with dissolved glass at the end of thirty

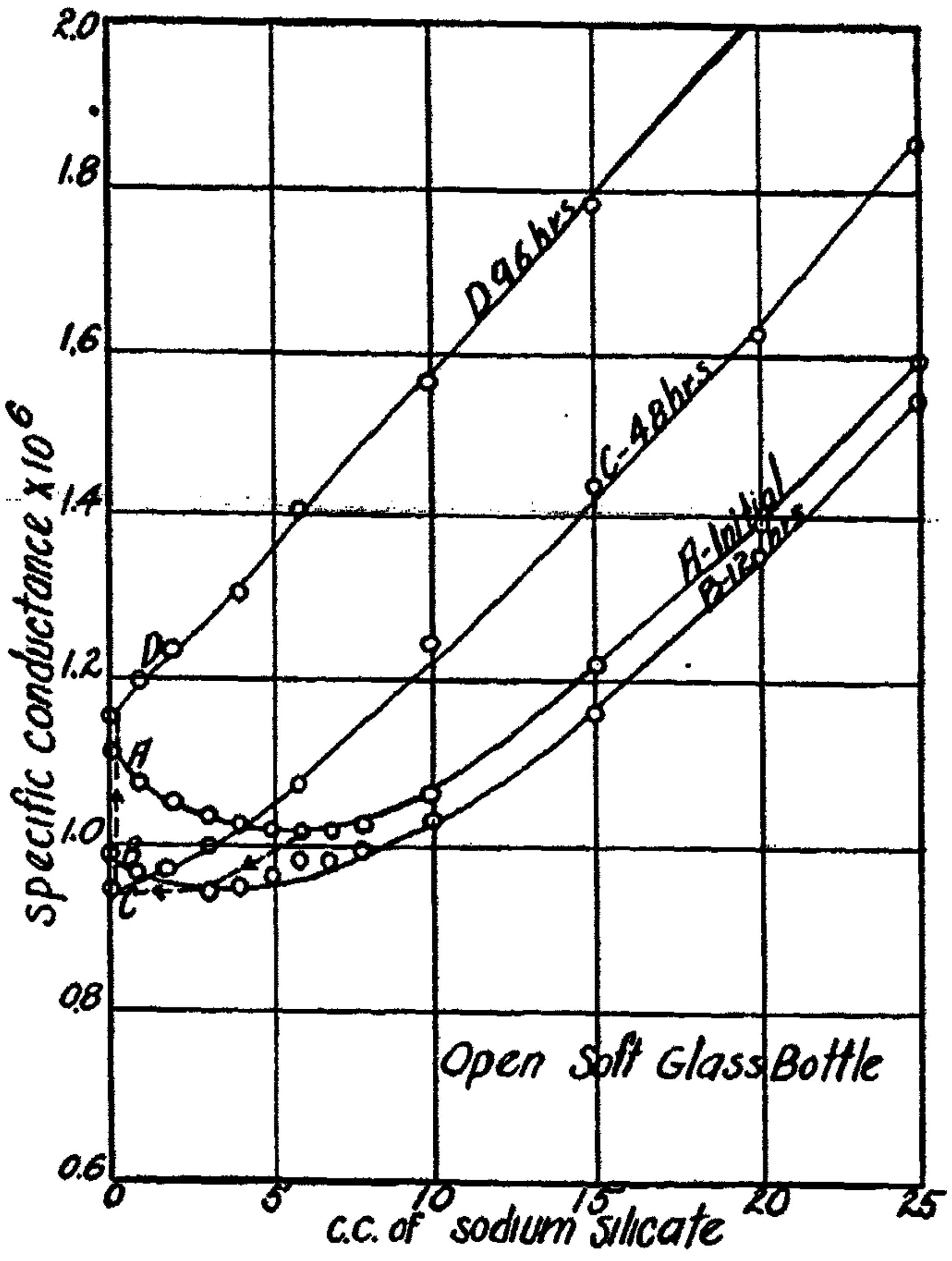

Fig. 6. Change in Carbon Dioxide Content of Conductivity Water with Time of Storage in Open Soft Glass Bottles at 25°C.

days and the conductance is now due to the products of the reaction. With soft glass the action is much faster. There is no carbonic acid present at the end of ninety-six hours. Water collected hot directly in a soft glass bottle showed no depression with sodium silicate solution, indicating the presence of no carbonic acid.

Parallel with these a bottle of water was stirred vigorously with a Pyrex glass stirrer. The time required for complete removal of carbon dioxide was forty-eight hours. Further experiments were run by bubbling hydrogen and nitrogen through the water. This had the effect of reducing the partial pressure of the carbon dioxide above the water, thereby decreasing the solubility of the carbon dioxide in the water; also it had the effect of increasing the rate of solution of the glass. Merely shaking the water in the flask gave a corresponding decrease in conductance. A summary of the results is given in table 1.

TABLE 1

	TIME	INITIAL CONDUCTIVITY	FINAL CONDUCTIVITY
	hours		
Hydrogen	4	0.85×10^{-6}	0.47×10^{-6}
Nitrogen	4	0.96×10^{-6}	0.45×10^{-6}
Shaking	1	1.17×10^{-6}	0.93×10^{-6}

A direct measure of the solubility of Pyrex glass was attempted by evaporating in a platinum dish 10 liters of conductivity water which had been standing in a Pyrex bottle for fifteen months. The initial conductance was 1.0×10^{-6} and the final 1.23×10^{-6}. Conductometric titration with very dilute alkali showed that no carbon dioxide was present. The total solids obtained was 10.9 mg., of which 4.8 mg. was silica.

The need and application of a correction for this "solution of glass" in measuring the conductivity of very dilute solutions of electrolytes or even hydrogen-ion concentrations can clearly be seen from figures 2, 3, and 4. For strong acids a positive correction is needed, rather than the "normal" water correction or the zero correction assumed in the theory of the carbonic acid correction; for a basic solution a slight negative one is needed. The conductance of neutral salts is not affected abnormally by the presence of such small amounts of sodium silicate. The magnitude of the ideal correction could be determined by the solubility of the glass, the equilibrium relations with sodium carbonate, silicate, and bisilicate ions, and the mobilities of the ions involved. The uncertainty of the values and complexity of such calculations is at once evident when it is remembered they can be carried out only by a series of approximations. However, if the condition of the water is known, estimation of the approximate correction can be made with less difficulty.

From the laws of diffusion, it is known that if fresh conductivity water is put in a glass cell, the rate of solution or decomposition of glass will at first be comparatively large, owing to the high concentration gradient from the surface of the glass to the interior of the liquid. This gradient is maintained for a while by the effectual removal of the sodium silicate in the solution by reaction with the comparatively high concentration of carbonic acid. The complications and errors arising from the use of glass apparatus can easily be seen and one can see that water of 0.4×10^{-6}, or better, should be used if carbon dioxide can be excluded. If higher conducting water is to be stored some time before use, it might even be advisable to allow it to come to a carbonic acid-free condition (this can be determined by conductometric titration with dilute alkali), otherwise, worse complications set in because the relative amounts of carbon dioxide and silicates are not known exactly. The best way to eliminate such errors and complications if platinum is not available, is to use quartz, which is acted on only slightly by electrolytes and water, or wax-coated vessels for collection and storage of the water and solutions. Some of the newer types of bakelite preparations show some promise. A carbonic acid-free condition can nearly be obtained by bubbling nitrogen or hydrogen through until no further decrease in conductance is observed.

If, as was supposed by the earlier investigators, the sodium silicate is highly hydrolyzed in dilute solution to sodium hydroxide and colloidal silicic acid, one would expect the slope of the curves for sodium hydroxide to be less than the one for water, owing to depression of hydrolysis by the OH^- ion and to adsorption by the colloidal silicic acid. If, as suggested by Haag (7) the hydrolysis of the sodium metasilicate is represented as follows:

$$\begin{array}{cccccc}
Na_2SiO_3 & + H_2O & \leftrightarrows & NaOH & + & NaHSiO_3 \\
\upharpoonleft\downharpoonright & & & \downarrow\uparrow & & \downarrow\uparrow \\
2Na^+ + SiO_3^{--} & & & Na^+ + OH^- & & Na^+ + HSiO_3^-
\end{array}$$

then the limiting value of the hydrolysis will be 0.5. This can be assumed to be very nearly true, for it has been quite definitely demonstrated by Haag that practically all the silica in very dilute solutions of that ratio exists in the form of $HSiO_3^-$ ions and does not readily form colloidal particles. Since $NaHSiO_3$ is a highly ionized salt, the effect of such small OH^- ion concentrations in decreasing the hydrolysis is small, while its effect on the secondary ionization of silicic acid existing as hydrosilicate ions or crystalloidally is comparatively greater and the conductance will rise abnormally.

In the conductivity water, which can be considered a solution of carbonic acid, and in the hydrochloric acid solutions effectually what we have happening is an exchange of the slow-moving sodium ion for a fast-moving hydrogen ion, which results in a lowering of the conductance. This can be offered as an explanation of the maximum found in the data for very dilute solutions of strong acids.

If glass, as previously suggested, should be dissolved in the form of silicates of sodium, rich in silica, and practically all the silica is in the crystalloidal state as shown by Harman, then one can rightfully assume there is an equilibrium established between the crystalloidal silica, SiO_3^{--} ions, $HSiO_3^-$ ions, and the alkali. As an acid is added, an amount of SiO_3^{--} ions equivalent to the sodium hydroxide *formed* on hydrolysis plus half the sodium in the unhydrolyzed silicate is converted to $HSiO_3^-$ ions. On further addition these ions are converted to silicic acid which first separates out colloidally and then changes largely to the crystalloidal state. Thus it is seen that in making an ideal correction for the "solution of glass," one must take into account both the alkali and the silica, for even though, as Morey (12) has concluded from his isothermal saturation curves, there can be no true solubility of the silicate at ordinary temperatures, but rather a decomposition by the water, forming products which contain vanishingly small amounts of silica, the fact still remains that a large part of the substance dissolving is silica which furnishes silicate ions, bisilicate ions, and colloidal electrolyte. The excess silica may give rise to further complications owing to the formation of these colloidal electrolytes originally suggested by McBain (13) and more specifically applied to silicate solutions by Harman (8). Other substances undoubtedly dissolve which have their influence, but under conditions ordinarily met with in conductance or hydrogen-ion work, the solution of alkali and silica will be the greatest disturbing factor. Any reliable work carried out in glass apparatus on very dilute solutions, whether it be conductance, electrode potentials, or hydrogen-ion concentration, should take into consideration a correction for the "solution of glass."

SUMMARY

1. Measurements of the effect of small amounts of sodium silicate, such as are dissolved from glass, on the conductance of conductivity water of different initial conductivities and on very dilute solutions of hydrochloric acid, sodium hydroxide, and potassium chloride have been made.

2. The change in the nature of impurities in conductivity water with different methods of collection and time of storage in Pyrex and soft glass containers has been demonstrated.

3. It has been shown that in addition to a "normal" water correction, taking into consideration the carbonic acid present, there must also be applied a correction for the "solution of glass."

4. The correction for the "solution of glass" will depend upon the kind of glass used in storage and measurements of the conductivity water and the solutions, on the time of such storage and measurements, and on the nature of the electrolyte worked with. The magnitude of the ideal correction could be calculated from the ionic mobilities and equilibrium relations of

the substances formed by the interaction of the electrolyte with the carbonic acid, sodium carbonate, bisilicate, and crystalloidal silica found to be present. The approximate correction can best be obtained by taking into consideration the alkali, carbonates, and carbonic acid, the proportion of which can be approximately determined by conductometric titrations.

In conclusion I wish to express my thanks to Professors C. L. von Ende and J. A. Kostalek for the helpful suggestions offered and for placing the facilities of the Department at my disposal. The assistance and suggestions from the other members of the Department is also appreciated.

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THE DISTRIBUTION OF METHYLAMINE BETWEEN WATER AND CHLOROFORM AND THE EXISTENCE OF METHYLAMINE COMPLEXES OF THE METAL-AMMINE TYPE

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OBJECT OF THE INVESTIGATION

The purpose of this investigation was the determination of the ratio of distribution of monomethylamine between water and chloroform and the presentation of evidence for the existence and composition of its complex with a copper salt.

The existence and constitution of complexes of ammonia with salts have been shown in many cases; an excellent summary has been given by Miss M. M. J. Sutherland (1). There is some evidence that amines form complexes similar to these ammines, though very few data are recorded in the literature. E. Thiele (2) found that copper oxide dissolved in aqueous monomethylamine solution to form a solvent for cellulose. Von Euler (3) found that silver salts and methylamine react to form the complex ion $[Ag(CH_3NH_2)_2]^+$, having a dissociation constant at 25°C. of 2.45×10^{-7}. Wuth (4) came to a somewhat different conclusion of this same complex, as a solid, from his solubility investigations of silver chloride and bromide in methylamine solution. Olmer (5) has determined the solubility of silver oxide in aqueous methylamine.

One of the most direct determinations of the constitution of ammines in solution is furnished by the application of the distribution law. Nernst (6) pointed out that a constancy in the distribution ratio can exist only between those molecules of the distributed substance which are in the same molecular condition in the two phases. If the distributed molecules undergo reversible chemical combination, association, or dissociation, this effect must be taken into account before the constancy in the distribution can be detected. Conversely, it is clear that a knowledge of the distribution ratio could be used for the determination of the degree of chemical combination or of dissociation in either of the two phases. Moreover, if the distributed substance remains in the form of simple molecules in one phase and undergoes a change in the second phase, the extent of combination of the distributed substance with an added material in the second phase could be determined from the change in the distribution ratio caused by this added substance. Thus, Dawson and McCrae (7), by observing the change in the distribution ratio of ammonia between water and chloroform upon the addition of a definite amount of copper salt to the water, were able to show the existence of a complex ion containing four molecules of ammonia per atom of copper.

Applying this consideration to methylamine, if the distribution coefficient, uncorrected for any dissociation of methylamine in the water layer, is defined by the relation

$$P = C_1/C_2$$

for pure water, the relation for an aqueous salt solution (e.g., copper salt), becomes

$$P' = C_1'/C_2$$

where C_1' is the molal concentration of the methylamine in the aqueous salt solution and C_1 and C_2 are the molal concentrations in pure water and in chloroform, respectively. It follows that the amount of methylamine in the water layer uncombined with the copper salt and free to maintain the equilibrium with that in the chloroform layer will be given by the distribution coefficient for pure water at the corresponding concentration of methylamine in the chloroform layer, i.e., by

$$C_1 = C_2 \cdot P$$

while the remaining methylamine, that is, the amount combined with the copper salt, is given by

$$C_1' - C_1 \text{ or } C_1' - C_2 \cdot P$$

Hence, if C_x is the concentration of copper ion in the water, the number of molecules of methylamine combined with one copper ion will be given by the relation

$$\frac{C_1' - C_1}{C_x}$$

In assuming that the concentration C_1 calculated by this method is the same as it would have been if no copper salt were present, it is necessary to presuppose that the addition of copper salt has *no* effect upon the respective physical properties of water and chloroform and that it is soluble only in the water phase.

It is also necessary to neglect the purely physical effect of the copper ions, the anions, or any complex ions formed upon the solubility of methylamine in water. If the concentration of these ions is small, the salting-out effect will be small, of course. Dawson and McCrae (8) studied the effect of a large number of salts upon the distribution of ammonia between water and chloroform; they came to the conclusion that the copper sulfate used in their distribution experiments decreased the solubility of ammonia in water. By analogy, it may be reasoned that it would have a similar salting-out effect upon the solubility of methylamine in water. In this investigation, the copper salt concentration is kept small, and hence the salting-out effect will be small; this effect has not been considered in making the calculations necessary to determine the constitution of the complexes formed.

THE DISTRIBUTION COEFFICIENT

Since the proposed method of investigation of the complexes requires an accurate knowledge of the distribution ratio of methylamine between water and chloroform, a search in the literature for this ratio was made. Smith (9) gives a value of 5.848 at 25°C. for the ratio C_1/C_2, as the mean of several determinations in which the methylamine concentrations in the water layer varied from 2.625 to 27.4 millimoles per liter. Moore and Winmill (10) give a value of 8.00 at 25°C. as the mean of two determinations in which the methylamine concentrations in the water layer were 0.1203 and 0.1312 gram-equivalents per liter. Both of these ratios were expressed in terms of volume concentrations.

The lack of agreement in the values of C_1/C_2 and the limited range of concentration over which the ratio has been determined made it necessary to determine accurately the ratio over a greatly extended concentration range before the composition of the ammine complexes could be determined.

Experimental procedure

The method consisted in analyzing both layers, after establishment of equilibrium, between an aqueous solution of methylamine and chloroform. Hantzsch and Sebaldt (11) have shown that such an equilibrium is quickly reached. A convenient volume of the aqueous methylamine solution, usually 150 cc., was placed with 200 cc. of chloroform in a Pyrex cylinder of approximately 500 cc. capacity. The cylinder was equipped with a ground glass stopper and two capillary stop-cocks, one sealed in near the bottom of the cylinder for the removal of the chloroform layer and one sealed in near the center for the removal of the water layer. The cylinder and contents were rotated in a water thermostat at 25° ± 0.01°C. for a period of four and one-half to six and one-half hours at a speed of sixteen to seventeen revolutions per minute.

After rotation, the cylinder was allowed to stand in an upright position in the thermostat for one and one-half hours to effect a separation of the layers. To eliminate loss of methylamine by evaporation, samples were forced by pressure of dry air into previously weighed glass-stoppered

Erlenmeyer flasks containing a known amount of standard sulfuric acid and, in the case of the chloroform layer analysis, enough distilled water to cover the chloroform layer. The flask and contents were weighed immediately. In the case of the water layer, it was possible to take a sample only slightly in excess of the amount required to neutralize the acid, the excess being subsequently titrated with 0.05 *M* or 0.005 *M* acid, depending upon the methylamine excess.

The method yielded reproducible results, indicating that no methylamine was lost by this procedure. In all determinations duplicate samples were taken from each layer, the aqueous samples weighing about 30 to 40 g. and the chloroform samples about 80 to 100 g. The total divergence from the mean for the samples from both layers was usually less than 0.1 per cent, the water layer yielding the most reproducible values. All titrations were made by weight, using methyl orange with the chloroform layer and methyl red with the aqueous layer. Methyl red is removed almost completely from water by chloroform in contact with it; hence methyl orange was used there.

Although Abbot and Bray (12) reported that an emulsion of water and chloroform can be broken up by slow rotation, it was found in this investigation that the turbidity refused to disappear even on long standing. To break up the emulsion, the samples were forced through two fine "fritted" glass filters in series with the discharge tubes. About 25 cc. of the equilibrium solutions was first forced through the filters and discarded before the sample for analysis was taken. Thus the filters could not alter the methylamine concentration of the sample proper.

Preparation of materials

The 0.5 and 0.05 *M* sulfuric acid solutions were prepared from C. P. sulfuric acid and standardized against 100 per cent sodium carbonate dried for two hours at 140°C. The usual precautions for highest accuracy were observed.

The 0.01 *M* sodium hydroxide was prepared from C. P. sodium hydroxide and standardized by weight against the 0.05 *M* sulfuric acid, using methyl red as an indicator.

The chloroform was Baker and Adamson quality chloroform, repurified by shaking with 10 per cent sodium hydroxide, washing three times with distilled water, shaking with 5 per cent sulfuric acid, washing again three times with distilled water, drying with a mixture of calcium oxide and calcium chloride, and then distilling. The distilled product was stored in well-stoppered dark bottles under an atmosphere of carbon dioxide to prevent oxidation. Samples kept thus for a week showed no effect on potassium iodide nor changed a color indicator. This observation is contrary to the observation of Dietrich (13).

Methylamine solutions were prepared by passing the gas into distilled water. The gas was liberated in an all-glass generator by the interaction of methylamine hydrochloride and concentrated sodium hydroxide solution. The methylamine hydrochloride was a purified product which, upon drying in a vacuum, had a melting point of 234°C. The final product gave *no* test for ammonia, dimethylamine, or trimethylamine.

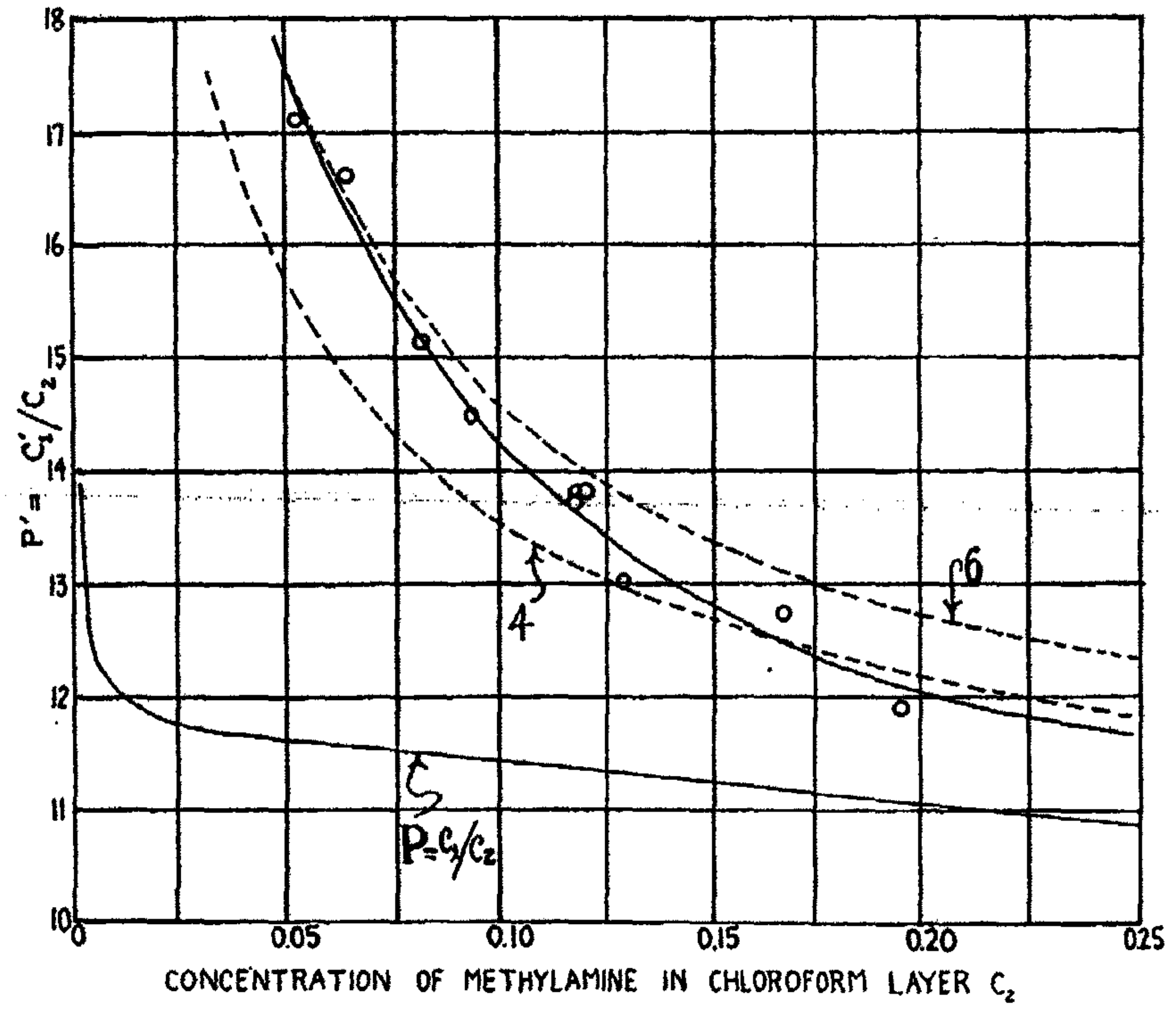

FIG. 1. DISTRIBUTION CURVE FOR METHYLAMINE BETWEEN 0.05 *M* COPPER SULFATE SOLUTION AND CHLOROFORM

EXPERIMENTAL RESULTS

The data and results of the distribution ratio determination are given in table 1. The last column contains the values of the true distribution ratio,[1] K_D, based upon calculations involving the dissociation of methylamine in water solution. The value of the dissociation constant, K_m, was taken as 4×10^{-4}, this being the most probable value derived from the published values of Bredig, of Bruni and Sandonnini, and of Harned and Benton (14).

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[1] $K_D = \frac{2C_1 + K_m \pm \sqrt{(K_m^2 + 4K_mC_1)}}{2C_2}$, where C_1 and C_2 are the molal concentrations of methylamine in the aqueous and the chloroform layers, respectively.

TABLE 1

Distribution of methylamine between water and chloroform

RUN	MOLALITY C_1 (water layer)	MOLALITY C_2 ($CHCl_3$ layer)	$P = C_1/C_2$	K_D
1	0.02113	0.001521	13.89	12.10
2	0.06876	0.005611	12.25	11.35
3	0.10151	0.008380	12.11	11.38
4	0.08601	0.007120	12.08	11.28
5	0.2003	0.01682	11.90	11.39
6	0.2484	0.02104	11.80	11.34
7	0.3793	0.03242	11.70	11.32
8	0.5837	0.05018	11.63	11.33
9	0.6850	0.05940	11.53	11.25
10	0.7917	0.06861	11.53	11.28
11	0.9741	0.08473	11.50	11.26
12	1.1157	0.09788	11.40	11.18
13	1.2773	0.1126	11.34	11.14
14	1.4714	0.1302	11.30	11.11
15	1.5563	0.1379	11.28	11.10
16	1.6858	0.1501	11.23	11.06
17	1.7485	0.1551	11.27	11.10
18	1.9960	0.1785	11.18	11.02
19	2.0384	0.1834	11.11	10.96
20	2.3779	0.2157	11.02	10.88
21	2.6180	0.2402	10.90	10.76

TABLE 2

Distribution of methylamine between aqueous copper sulfate solutions and chloroform

Concentration in molalities

RUN	C_1' (in $CuSO_4$ solution)	C_2 (in $CHCl_3$)	P' (C_1'/C_2)	P (C_1/C_2)	C_1 ($C_2 \cdot P$)	C_x ($CuSO_4$)	$\frac{C_1' - C_1}{C_x}$
1	0.9037	0.05281	17.11	11.58	0.6115	0.0519	5.63
2	1.0523	0.06334	16.61	11.53	0.7303	0.0519	6.20
3	1.2238	0.08081	15.14	11.46	0.9261	0.0525	5.67
4	1.3494	0.09318	14.48	11.42	1.0641	0.0527	5.41
5	1.6093	0.1171	13.74	11.36	1.3302	0.0532	5.25
6	1.6238	0.1177	13.80	11.34	1.3347	0.0533	5.42
7	1.6547	0.1197	13.82	11.35	1.3586	0.0533	5.56
8	1.6793	0.1291	13.01	11.31	1.4601	0.0534	4.10
9	1.9322	0.1517	12.74	11.24	1.7051	0.0539	4.21
10	2.3399	0.1967	11.90	11.11	2.1853	0.0547	2.83

These values of K_D were plotted to large scale as functions of the concentration of methylamine in the chloroform layer. This dependency is given by the linear equation:

$$K_D = 11.39 - 2.32\, C_2$$

The variation shown is not explained by the distribution law; it is in accord, however, with the findings of Dawson and McCrae, of Bell and Fields, and of Occleshaw (15) on the distribution coefficient of ammonia between water and chloroform.

Complex formation with copper sulfate

Experimental procedure.—A stock solution approximately 0.5 molal in copper sulfate was prepared from carefully recrystallized salt. This solution, in any given determination, was diluted by adding to 15 g. of it exactly 150 g. of aqueous methylamine solution; this produced a solution approximately 0.05 molal in copper sulfate. Since part of the methylamine diffuses out of the water layer into the chloroform to establish equilibrium, the water layer loses weight by this amount. The actual concentration of copper sulfate in the water layer could be calculated from the known weight of aqueous solution and of chloroform placed together into the cylinder and the analytically determined distribution coefficient.

The two layers were analyzed as before with the same precautions. Methyl orange had to be used as indicator even with the water layer, because the copper hydroxide formed upon titration with acid masked the methyl red color change.

Experimental results.—The results of this series of determinations are presented in table 2. Since it was shown in table 1 that the uncorrected distribution coefficient for pure water and chloroform, $P = C_1/C_2$, varied with concentration of methylamine, it was necessary to ascertain the value of P corresponding to each concentration in the chloroform layer when the copper salt is present in the aqueous layer. This permits a calculation to be made of the concentration of the methylamine in the water layer which would exist if no salt were present and permits the calculation of the number of moles of methylamine in combination with the cupric ion. For this purpose the values of P from table 1 were plotted against the concentration, C_2, of methylamine in the chloroform layer. The values of P in column 4 of table 2 were taken from this curve. The last column of this table contains the calculated number of moles of methylamine combined per mole of copper sulfate; this ratio is not constant, *the value decreasing as the concentration of methylamine increases.* The data for copper sulfate are plotted in the accompanying figure; in addition there are included two other curves, shown dotted and marked 4 and 6, which represent the values of the distribution ratio that would be required if four and six molecules, respectively, of methylamine were united with one mole of copper sulfate (neglecting any other effect). An inspection reveals that the number of moles of combined methylamine per mole of copper sulfate *approaches six as a limit.* Since it would be extremely unusual for the cupric ion to combine with six moles of methylamine in a dilute solution and then liberate part of this in a more concentrated solution of the amine, it appears that the evidence supports the conclusion that methylamine is capable of uniting with the cupric ion in the ratio of 6 to 1 to form a complex ion with no indication that this complex dissociates appreciably even in dilute solution.

SUMMARY

1. The distribution ratio of methylamine between water and chloroform has been determined over a range of concentrations in the water layer from 0.02113 to 2.6180 molal.

2. The distribution ratio is not constant, except in the very dilute region (after correcting for dissociation); the ratio decreases with increasing concentration.

3. Methylamine forms a complex of the ammine type with the cupric ion, the number of moles of methylamine to one cupric ion approaching *six* as a maximum. The number in more concentrated methylamine solution *appears* to decrease.

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THE ACIDITY OF ORGANIC ACIDS IN METHYL AND ETHYL ALCOHOLS

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The investigation described in this paper was undertaken for the purpose of studying the changes in the acidity constants of certain organic acids as related (1) to changes in the character and position of substituted groups, and (2) to changes in the character of the solvent. The term acidity constant is used here in the same sense as it is defined by Brönsted (1). The methods employed in the study follow closely after those used by Michaelis and Mizutani (2). In short, it consists of measurements of the potential difference between a saturated potassium chloride calomel half-cell and a hydrogen electrode immersed in ethyl or methyl alcohol–water solutions of equimolecular concentrations of organic acids and their sodium salts. From such measurements the "reduced dissociation constants," as defined by Michaelis and Mizutani, or the equivalent values of K_A in Brönsted's equation

$$K_A = A_{\mathrm{H}^+} \cdot \frac{C_B}{C_A}$$

can be calculated. The activity of hydrogen ion, A_{H^+}, is assumed to be the same for two solutions of an acid, one in water and the other in alcohol or an alcohol–water mixture, when these show the same potential toward the normal hydrogen electrode. The limitations of this assumption, and of the method in general, are fully realized.

EXPERIMENTAL PROCEDURE

All materials were purified by the usual methods, and the usual precautions of E. M. F. measurements were observed. The Hildebrand bubbling electrode was used for all measurements of potential involving the hydrogen electrode. The electrodes were platinized lightly according to the directions of Popoff, Kunz, and Snow (3). Hydrogen was prepared by

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[1] This paper was constructed from a thesis offered by William L. Bright in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Indiana University. Further details of the investigation are contained in the thesis, which was filed in the library of Indiana University, June, 1932.

the electrolysis of a solution of sodium hydroxide. A Leeds and Northrup Type K potentiometer and Type R reflecting galvanometer were used in the determination of the potentials.

A 0.1 *N* solution of the acid under consideration was prepared by dissolving the required amount of carefully weighed acid in absolute alcohol. The acid was weighed, using all the usual precautions and making the usual corrections, on a microanalytical balance. Flasks of 100 ml. capacity and carefully calibrated were used in making up these solutions. In making up the solutions of varying proportions of alcohol, 20 ml. of the 0.1 *N* acid solution and 10 ml. of a 0.1 *N* aqueous sodium hydroxide solution were added to a 100-ml. flask from a calibrated burette. The quantities of alcohol and water necessary to give the desired ratio of these solvents were then added.

The E. M. F. was read at five minute intervals, until two consecutive readings did not vary more than 0.2 millivolt. Equilibrium at the hydrogen electrode was usually reached in about twenty minutes. All measurements of E. M. F. were made in an air-bath at 25° (±1°)C. For the calculation of the pH of solutions, the values of the potential of the calomel half-cell at the temperature of the experiment have been taken from tables prepared by Clark (4). Other values used in calculating the pH of solutions for which the quinhydrone electrode was used were also obtained from Clark's tables.

In the few cases where our determinations overlap those made by Michaelis and Mizutani, we have been interested in checking our equipment and procedure against theirs. The two sets of values for the pH of the solutions are not quite in agreement, because it appears that Michaelis and Mizutani have used a different value for the E. M. F. of the saturated potassium chloride calomel half-cell than that given by Clark. Thus, at 18°C. Clark's value for this half-cell is 0.251 volt, while that used by Michaelis and Mizutani appears to be 0.2498 volt.

RESULTS

The results of the determinations are shown in table 1. The values of pH for solutions in 100 per cent alcohol are those obtained by extrapolation, an unavoidable method which is subject, of course, to some error. The points on the curve for zero per cent alcohol may be taken either from the observed pH values, or they may be based upon the convention, which is usually followed, that pK_A for aqueous solutions is equal to the pK of dissociation. Comparisons of the values obtained by the use of the quinhydrone and hydrogen electrodes have been made for the solutions of benzoic acid. The quinhydrone electrode was used in the study of the nitrobenzoic acids, since the hydrogen electrode did not give equilibrium readings in these solutions.

TABLE 1

Measurements of pH in alcohol–water mixtures

ALCOHOL PER CENT BY VOLUME	BENZOIC	BENZOIC (Quinhydrone)	o-TOLUIC	m-TOLUIC	p-TOLUIC	o-AMINOBENZOIC	m-AMINOBENZOIC	p-AMINOBENZOIC	o-HYDROXY-BENZOIC	m-HYDROXY-BENZOIC	p-HYDROXY-BENZOIC	o-CHLOROBENZOIC	m-CHLOROBENZOIC	p-CHLOROBENZOIC	o-NITROBENZOIC (Quinhydrone)	m-NITROBENZOIC (Quinhydrone)	p-NITROBENZOIC (Quinhydrone)	PROPIONIC	n-BUTYRIC	ISOBUTYRIC	n-VALERIC	ISOVALERIC	n-CAPROIC	ISOCAPROIC
Ethyl																								
0										4.04	4.51							4.68	4.83	4.77	4.74	4.65	4.80	4.75
20	4.48	4.48	4.32	4.62	4.84	5.28	4.97	5.23	3.33	4.54	4.97	3.42			2.63			5.23	5.24	5.29	5.41	5.24	5.20	5.22
40	5.31	5.13	5.21	5.37	5.46	5.87	5.49	6.06	3.73	5.24	5.72	4.22	4.79		2.77	3.60	3.95	5.86	5.84	5.94	6.05	5.90	5.83	5.94
50	5.64	5.44	5.61	5.72	5.80	6.20	5.83	6.43	4.01	5.61	6.07	4.55	5.11	5.20	3.59	4.32	4.15	6.16	6.18	6.33	6.39	6.24	6.21	6.28
70	6.24	6.03	6.32	6.40	6.36	6.90	6.52	7.19	4.62	6.36	6.80	5.18	5.72	5.81	4.20	4.85	4.69	6.80	6.83	7.00	7.03	6.87	6.85	6.95
80	6.61	6.30	6.67	6.75	6.73	7.29		7.60	4.90	6.73	7.23	5.51	6.06	6.13	4.52	5.17	5.00	7.19	7.21	7.32	7.34	7.23	7.21	7.27
90	6.91	6.52	7.01	7.14	7.08	7.67		7.97	5.27	7.11	7.66	5.82	6.39	6.49	4.85	5.43	5.28	7.56	7.56	7.70	7.65	7.57	7.53	7.63
95		6.92		7.32	7.32	7.84		8.16	5.46	7.30	7.88	5.98	6.54	6.69	4.98	5.57	5.47	7.76	7.74	7.90	7.76	7.74	7.71	7.81
100*	7.29	7.10	7.34	7.50	7.36	8.00	7.54	8.38	5.61	7.48	8.10	6.14	6.70	6.84	5.14	5.70	5.54	7.96	7.90	8.08	7.98	7.92	7.88	7.98
Methyl																								
20	4.41											3.20			2.70	3.56		5.19	5.14	5.54	5.29	5.15	5.19	5.14
40	4.92											3.78	4.37		3.01	3.86		5.64	5.61	5.97	5.79	5.64	5.66	5.62
50	5.15											4.02	4.70		3.16	4.04	4.16	5.84	5.88	6.23	6.04	5.89	5.91	5.90
70	5.72											4.63	5.26	5.55	3.70	4.46	4.51	6.41	6.41	6.70	6.54	6.41	6.44	6.40
80	5.97											4.94	5.56	5.74	3.83	4.68	4.74	6.68	6.64	6.96	6.83	6.68	6.64	6.61
90	6.12											5.20	5.77	5.91	4.25	4.81	4.97	6.94	6.96	7.17	7.09	6.92	6.85	6.93
95	6.37											5.31	5.90			5.01	5.12	7.06	7.09		7.19	7.04	7.13	7.04
100*	6.50											5.48	6.02	6.14	4.52	5.12	5.20	7.20	7.24	7.40	7.33	7.29	7.26	7.16

* Extrapolated. All measurements are by hydrogen electrodes except where quinhydrone is indicated.

DISCUSSION OF RESULTS

Variations of K_A with differences in the structure of the acids

The acidity constants of the substituted benzoic acids show the effect of (1) the nature of the substituent, and (2) its position in the benzene nucleus with respect to the carboxyl group. We may interpret these effects in the light of Kharasch's (5) measurements of the relative electronegativities of different organic radicals. Accepting his meaning of the term electronegativity, it appears that the more electronegative the atom or group (R) attached to the hydroxyl radical (ROH), the more readily hydrogen is removed from its linkage with oxygen; thus, phenol is a stronger acid than methyl alcohol. In keeping with the interpretation

TABLE 2

The acidity constants of substituted benzoic acids in methyl and ethyl alcohols[*]

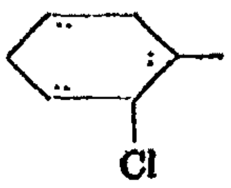
I ACID	II pK_A[†]	III $pK_A - pK_A$(Benzoic acid)
Ethyl alcohol		
o-Nitrobenzoic	5.14	−2.15
p-Nitrobenzoic	5.54	−1.75
Salicylic	5.61	−1.68
m-Nitrobenzoic	5.70	−1.59
o-Chlorobenzoic	6.14	−1.15
m-Chlorobenzoic	6.70	−0.59
p-Chlorobenzoic	6.84	−0.45
Benzoic	7.29	0.00
o-Toluic	7.34	0.05
p-Toluic	7.36	0.07
m-Hydroxybenzoic	7.48	0.19
m-Toluic	7.50	0.21
m-Aminobenzoic	7.54	0.25
o-Aminobenzoic	8.00	0.71
p-Hydroxybenzoic	8.10	0.81
p-Aminobenzoic	8.38	1.09
Methyl alcohol		
o-Nitrobenzoic	4.52	−1.98
m-Nitrobenzoic	5.12	−1.38
p-Nitrobenzoic	5.20	−1.30
o-Chlorobenzoic	5.48	−1.02
m-Chlorobenzoic	6.02	−0.48
p-Chlorobenzoic	6.10	−0.40
Benzoic	6.50	0.00

[*] The acids are listed in the order of decreasing acidity.

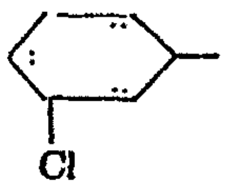
[†] Uncorrected for ion activity instead of ion concentration.

below, this may mean that the presence of the electronegative atom or group causes oxygen (in OH) to act less electronegatively toward hydrogen and, therefore, to hold hydrogen less firmly. Concerning substitutions for hydrogen in the radical R, Kharasch finds that the more electronegative the substituent, the less readily this radical combines with hydrogen. He takes this to mean that R becomes less electronegative (toward hydrogen). The acidity constants of the substituted benzoic acids indicate that the more electronegative the substituent, the more readily hydrogen can be removed from its linkage with the RCOO— group. To apply Kharasch's reasoning to these results, it appears that we must assume that the substitution of an electronegative atom or group in R causes the RCOO— group to act less electronegatively toward hydrogen. There is the other view, of course, that the electronegative substituent causes the RCOO— group to act *more* electronegatively toward hydrogen. The increase in the strength of the acid may be due, in other words, to a change in the RCOO—H linkage which makes it more electrovalent and less covalent in character. Our present purposes do not require a discussion of the merits of these two points of view.

Kharasch finds that the presence of chlorine in any position in the phenyl group causes this group to exert a slightly decreased electronegativity toward any atom or group attached to it. This we may call the *primary* effect. This primary effect is modified somewhat by a *secondary* effect, which depends upon whether chlorine occupies the ortho, meta, or para position. The latter may be due to the orienting effect of chlorine upon the six "aromatic" electrons to which benzene owes its unsaturation.



Increased electronegativity

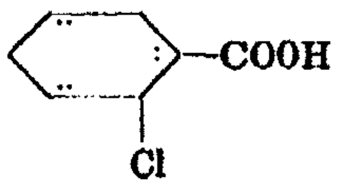


Decreased electronegativity

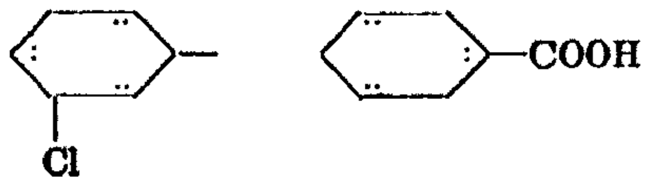
Increased electronegativity

Accordingly, chlorine in the meta position still further decreases the electronegativity of phenyl. Para and ortho chlorine, on the other hand, oppose the primary effect of the substitution of chlorine and slightly increase the electronegativity of the radical, although they do not overcome the decrease produced by the primary effect of chlorine. According to Kharasch's findings, the electronegativity of *p*-chlorophenyl is greater than the electronegativity of *o*-chlorophenyl; and both radicals are more electronegative than *m*-chlorophenyl. Chlorine in the para position acts, therefore, as a slightly less electronegative substituent than meta chlorine. Hence, *p*-chlorobenzoic acid should possess a smaller acidity constant than *m*-chlorobenzoic acid, in which both the primary and secondary effects act in the same direction. The acidity constant of *p*-chlorobenzoic acid falls next above that of benzoic acid. It appears, therefore, that in *p*-chlorobenzoic acid the secondary effect of chlorine in the para position almost neutralizes the primary effect.

The order of the acidity constant of *o*-chlorobenzoic acid is not what we might expect. Based upon Kharasch's order of electronegativity we should predict that *o*-chlorobenzoic acid should be intermediate, but instead it is stronger than either *p*-chlorobenzoic or *m*-chlorobenzoic acid. This discrepancy may be due to several causes. In the substituted benzoic acids, hydrogen is attached to an oxygen atom of the carboxyl group, which is itself a substituent in the phenyl group. If the carboxyl group is *very weakly* electronegative, as Kharasch believes, its effect is opposite to that of chlorine. For certain positions of chlorine the effects of the two substituents may be such as to decrease the electronegativity of phenyl toward chlorine. In such cases we must consider the electronegativity of chlorine toward phenyl as having been increased. In *o*-chlorobenzoic acid both chlorine and carboxyl may orient the six aromatic electrons of phenyl to the same positions:



The increased electronegativity of chlorine in the ortho position results in slightly increased strength for *o*-chlorobenzoic acid. In *m*-chlorobenzoic acid the orienting influences of carboxyl and chlorine are opposed:



In this case carboxyl slightly decreases the electronegativity of chlorine toward phenyl. This makes *m*-chlorobenzoic acid weaker than *o*-chlorobenzoic acid.

Methyl is less electronegative than chlorine. The tolyls are correspondingly more electronegative than the chlorophenyls. The toluic acids are weaker than benzoic. Their acidity constants fall in the order $o > p > m$. The order of the electronegativity of the tolyls is the same. Methyl in the ortho and para positions, as in the case of the substitution of chlorine, appears to increase slightly the electronegativity of phenyl. Since the primary effect of methyl-substitution also results in an increase in electronegativity, the two effects are additive in the *o*- and *p*-tolyls. Methyl in the meta position, however, slightly decreases the primary effect. Hence, *o*- and *p*-tolyl are more electronegative than *m*-tolyl.

Carboxyl should slightly increase the electronegativity of ortho or para methyl and decrease that of meta methyl. These differences in the electronegativity of methyl in its different positions account for the order of acidity constants.

The order of the acidity constants of the nitrobenzoic acids in ethyl alcohol is $o > p > m$. We cannot be certain of the order of the electronegativity of the nitrophenyls. The nitro group is more electronegative than chlorine; the nitrobenzoic acids are correspondingly stronger than the chlorobenzoic acids. If the hydroxyl radical has the same effect as methyl upon the electronegativity of the phenyl group, hydroxybenzoic acids should be weaker than benzoic acid. Kharasch states that both groups increase the electronegativity of phenyl, but he does not state that this is true for all positions of the hydroxyl radical. We find *o*-hydroxybenzoic (salicylic) acid stronger than benzoic acid, while the meta and para acids are weaker. In the hydroxybenzoic acids two hydroxyl groups are present, one in each substituent. The effect of the presence of these two groups on adjacent carbon atoms may have a profound influence upon the acidity constant of *o*-hydroxybenzoic acid. This effect may be of the same character as that which a hydroxylic solvent, such as water, exerts upon the dissociation of an acid dissolved in it.

The acidity constants of the aminobenzoic acids in ethyl alcohol are in the order $m > o > p$. This indicates that the amino radical has the opposite effect of chlorine and methyl upon the orientation of the "aromatic" electrons of phenyl. If the substitution of the amino group increases the electronegativity of phenyl, then the secondary effects of amino in the meta position will cause phenyl to be still more electronegative. Substitution of the amino radical in the ortho and para positions, however, will tend to decrease the electronegativity of phenyl. If this reasoning is correct, the order of electronegativity of the aminophenyls should be $m >$ (o and p). If the amino group is less electronegative than carboxyl, as seems likely, then the effect of carboxyl will be to make the ortho and para amino groups slightly less and the meta amino radical slightly more negative than when carboxyl is not present. These differences should make *m*-aminobenzoic acid slightly stronger than *o*- and *p*-aminobenzoic acids. The whole question of the acidity constants of the aminobenzoic acids, however, must be considered in the light of their amphoteric character.

The order of the acidity constants of the acids in methyl alcohol is the same as in ethyl alcohol. The acidity constants of the aliphatic acids (table 3) show no differences of any significance in either methyl or ethyl alcohol.

Variations of acidity constants of acids in water, methyl alcohol, and ethyl alcohol

The effect of the change of solvent upon the acidity constants of different acids (table 3) is not constant, and does not depend entirely upon the dielectric constants of the solvents. The change in K_A with change of medium is determined by the effect of the medium upon the ratio f_A/f_B of the activity coefficients of the uncharged acid and its anion. For monobasic organic acids, such as those which we have studied, the change from a medium of high to one of low dielectric constant should cause a slight decrease in the activity coefficient of the undissociated acid and an increase in the activity coefficient of the monovalent anion of the acid. These effects should result in a decrease in the acidity constant or an increase

TABLE 3

Changes of pK_A of acids with changes of solvent*

I ACID	II pK_A IN C_2H_5OH	III pK_A IN CH_3OH	IV pK_A† IN WATER	V pK_A II − IV	VI pK_A III − IV	VII pK_A II − III
o-Nitrobenzoic	5.14	4.52	2.63‡	2.51	1.89	0.62
p-Nitrobenzoic	5.54	5.20	3.40	2.14	1.73	0.34
Salicylic	5.61		2.97	2.64		
m-Nitrobenzoic	5.70	5.12	3.46	2.24	1.66	0.58
o-Chlorobenzoic	6.14	5.48	2.88	3.26	2.60	0.66
m-Chlorobenzoic	6.70	6.02	3.81	2.89	2.21	0.68
p-Chlorobenzoic	6.84	6.10	4.04	2.80	2.06	0.74
Benzoic	7.29	6.50	4.18	3.11	2.32	0.79
o-Toluic	7.34		3.90	3.44		
p-Toluic	7.36		4.37	2.99		
m-Hydroxybenzoic	7.48		4.08	3.40		
m-Toluic	7.50		4.25	3.25		
m-Aminobenzoic	7.54		4.79	2.75		
o-Aminobenzoic	8.00		4.97	3.03		
p-Hydroxybenzoic	8.10		4.54	3.56		
p-Aminobenzoic	8.38		4.92	3.46		
Propionic	7.96	7.20	4.88	3.08	2.32	0.76
n-Butyric	7.90	7.24	4.82	3.08	2.42	0.66
Isobutyric	8.08	7.40	4.81	3.27	2.59	0.68
n-Valeric	7.98	7.33	4.81	3.17	2.52	0.65
Isovaleric	7.92	7.29	4.77	3.15	2.52	0.63
n-Caproic	7.88	7.26	4.85	3.03	2.41	0.62
Isocaproic	7.98	7.16	4.84	3.14	2.32	0.82
Average				3.02	2.25	0.65

* Uncorrected for ion activities instead of ion concentration.

† $pK_A = pK_{\mathrm{Diss.}}$ for aqueous solutions.

‡ By graphical extrapolation.

in the values of pK_A. This is true for all the acids studied. The change in the acidity constants of the aliphatic acids (from one medium to another) is practically constant. But for the substituted benzoic acids the change of pK_A with change of medium is decidedly different for the different acids. In general it may be said that the change in pK_A increases with decreasing acidity. For those acids which are stronger than benzoic acid, the change in pK_A is less than for benzoic acid. For those which are weaker than benzoic acid, the change in pK_A is somewhat greater than or approximately the same as for benzoic acid. Even for the chain acids, a slight increase of the change is to be noted as the acidity decreases. In some cases (the hydroxybenzoic acids for example) there is a wide variation in the extent of the change of pK_A for the ortho, meta, and para isomers. In other cases, notably in the cases of the toluic acids, the effect is about the same for all three forms.

The relative order of the acidity constants of the different acids in ethyl alcohol, methyl alcohol, and water is not the same. This indicates that the effects, such as solvation, etc., upon the ratio of the activity coefficients of the acid and its anion in the three solvents are not comparable except for very closely related acids, such as those of the aliphatic series.

The difference between the negative logarithms of the basicity constants of water and ethyl alcohol can be measured by determining the difference between the negative logarithm of the dissociation constant of an acid in alcohol and the negative logarithm of the acidity constant of the same acid in alcohol. Kolthoff (8) has calculated this difference for salicylic and benzoic acids. His values are based upon the acidity constants of Michaelis and Mizutani, which he corrects for ion activities in place of ion concentrations. Using a similar method of calculation, our determinations for the three nitrobenzoic acids show a practically constant difference of 2.86 logarithmic units. This value is slightly higher than that obtained for salicylic and benzoic acids, in which cases our average difference was 2.7 logarithmic units. The latter figure is in agreement with Kolthoff's calculations. For the dissociation constants of the acids in ethyl alcohol and water we have used the data of Larsson (9), Goldschmidt (10), and Bjerrum and Larsson (11).

The determinations of the pK_A values for the nitrobenzoic acids were made, necessarily, by means of the quinhydrone electrode. We have measured the acidity constant of benzoic acid in water-alcohol mixtures by means of both hydrogen and quinhydrone electrodes. These results show a greater value for pK_A when the determination is carried out by means of a quinhydrone electrode than when the same value is measured by the hydrogen electrode. For the smaller concentrations of alcohol the differences in the two determinations of pK_A are negligible. But the extrapolated values of pK_A in 100 per cent alcohol show a difference of

0.19 logarithmic unit. Two similar determinations were also made of the pK_A of *p*-toluic acid; the difference between these was 0.15 unit. If we assume that the difference is of the same order for the nitrobenzoic acids, then the difference between the negative logarithms of the basicity constants of ethyl alcohol and water is $2.86 - 0.17 = 2.69$, which is the same value as we have found for the solutions of benzoic and salicylic acids.

The determinations of the relative basicity constants of different solvents are largely dependent upon accurate determinations of the dissociation constants of the acids dissolved in such solvents. Available data do not permit the determination of a single value for the difference between the negative logarithms of the basicity constants of water and methyl alcohol. So far, the determinations in ethyl alcohol are limited to five solutions, three of which are discussed in this paper for the first time.

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THE PHYSICAL CHEMISTRY OF FLOTATION. II

The Nature of the Adsorption of the Soluble Collectors

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It having been demonstrated that the angle of contact plays a very important part in determining the tenacity of attachment between a conditioned mineral surface and air, it becomes important to determine what factors determine the angle of contact. The magnitude of the angle of contact is fixed by the interfacial tensions of the three phases meeting at the line of triple contact mineral–air–water. Consequently, any factor having an effect on any one of the three surface tensions (or surface energies) will influence the angle of contact.

Every surface change may be expected to influence the surface energy, and thus no factor which influences the surface is without influence on flotation. Confusion has arisen in the literature owing to a lack of appreciation of this fact. Thus several writers, in emphasizing the importance of some one factor, have put forward their views as a complete theory of flotation. Even the writers of textbooks refer to the "contact angle theory of flotation," the "adsorption theory of flotation," etc.

Though no one factor is responsible for flotation, no factor is more important in flotation by soluble collectors than adsorption, and this is particularly true of adsorption at the solid surface. It has been shown (1) that air does not even partially replace water from clean surfaces of many common sulfide or gangue minerals. Metals and oxidized minerals behave similarly. It is only after the surfaces have acquired a coating of some "collector" that any displacement of water by air is possible at the surface. In the early application of flotation, the collectors used were oils and the surfaces were filmed by oil. Latterly, oils have been largely displaced as collectors by soluble non-oleaginous compounds, of which potassium ethyl xanthate is the most used. These, only, are considered in the present discussion. Under certain conditions unimolecular films are adsorbed by the minerals which then display a definite air avidity.

The orientation of the adsorbed molecule is all-important. If there be no polar group in the surface, contact with air (and displacement of water) is possible; if there be a polar group in the surface, contact with air is impossible. The lead, zinc, and copper salts of mandelic acid float very readily, though they are heavier than water. Mandelic acid contains two active groups; it is evident that both are orientated inwards in these salts, which are coördination compounds, and that the non-polar phenyl group is orientated outwards. The parent acid and the sodium salt are not collectors, however, for the sulfide minerals, proving that if they are adsorbed, there is an active group outermost. Other acids might be cited whose heavy metal salts float readily but which, themselves, do not act as collectors for the sulfide minerals. On the other hand, it is probably true that an acid, or its soluble salts, would not cause floatability if the heavy metal salts were not themselves readily floatable.

There are three aspects of the adsorption of soluble collectors which need examination.

1. Under what conditions does adsorption of the collector occur?
2. At what rate does adsorption occur?
3. If adsorption occurs, how is the angle of contact related to the constitution of the collector?

The first question is the most difficult to answer. Modern selective flotation is based upon the adsorption of a collector by one mineral and not by another, and an explanation must be sought for the differences between minerals in this respect. It is avoiding the issue to say that certain minerals attract the CS·S— group, though this is the customary method of accounting for adsorption. Incidentally, a valid explanation for the adsorption of xanthates by minerals would mark an important step forward in the theory of adsorption.

Of the theories which have been advanced, none has received more attention than that which postulates that adsorption is due to the formation of an insoluble compound on the mineral surface, and attention should be drawn to certain exceptions, lest it be taken for granted that the theory is established. Of the other theories, that which seeks to explain adsorption in terms of surface charges is also worthy of more consideration, but in the absence of definite experimental verification we have perforce to confine our attention to the former, the so-called "chemical" theory.

The chemical theory has been sponsored by Taggart and Gaudin and their collaborators. Gaudin, Haynes, and Haas (2) state that it has appeared more and more as their experimental work has progressed that the action of reagents on the flotation of sphalerite is strictly chemical. Taggart, Taylor, and Knoll (3) advance the generalization, "Simple chemical reaction underlies the functioning of the flotation reagents which control mineral collection, when these reagents are soluble in and act from solution in the water of the pulp." The proviso excludes collectors which are oils. It was not claimed that this generalization was substantiated exhaustively, and we therefore propose to discuss its usefulness as a working hypothesis.

A truly chemical theory implies that adsorption can occur only when the solution is saturated with respect to the adsorbed compound. As early as 1915, Paneth and Horowitz (4) pointed out that the amount of adsorption of certain radioactive elements is dependent on the degree of insolubility of their salts. This conclusion was confirmed by Fajans and Horowitz (5).

Evidence has been adduced by Taggart and Gaudin and their collaborators to show that there is a close connection between adsorption of xanthate at a mineral surface and the solubility of the xanthate of the metal in the mineral. Before the chemical theory can be accepted, it must be shown that this connection amounts to identity. In other words, it is necessary to show that the forces controlling adsorption are of the primary valence type.

The adsorbed film is surprisingly stable. Once adsorption has occurred, contact with air continues to be possible though the surface be washed with several changes of water. The alkali metal xanthate of the solution from which adsorption has occurred is extremely soluble in water; the heavy metal salts are of extremely low solubility. The heavy metal xanthates, moreover, flocculate readily about an air bubble and then float readily. There is thus some presumptive but not conclusive evidence that the adsorption is due to an insoluble film of the heavy metal salt.

Taggart (3) has stated, "We are rather inclined to think that in every case the solubility of the substance as a surface coating is somewhat less than that of the same substance independently put into solution, but I do not know." The solubility term used in describing adsorption may thus be different from that of the solubility of the same compound in bulk. It is of significance that the statement quoted arose in a discussion following the presentation by Taggart and his associates of a paper in which an attempt was implicitly made to explain "adsorption" in terms of primary chemical reactions. Does it not amount to an admission that the explanation was incomplete, i.e., that secondary valences must be considered?

Gaudin, Haynes, and Haas (2) evidently doubt the universal validity of the theory, for they state that though sphalerite can be floated by certain amines, no insoluble sulfides or zinc salts are formed by them. Apparently the substituted hydrazines may be classed with the amines.

Thus, though there is undoubtedly much evidence of a qualitative nature in favor of this theory of adsorption, there are many cases which apparently are exceptions. Upon examination some of the exceptional cases may later be explained on the grounds of oiling, but until such exceptional cases have been classified no sweeping generalization is justified.

Many cases have been cited in the earlier paper (1) which seem to conform to the chemical theory. Firstly, concerning the mode of action of activators, e.g., copper sulfate for sphalerite, the information available suggests that this follows the order of solubility of the sulfides. The chemical theory, if applicable here, would state that lead nitrate is effective in activating sphalerite because lead sulfide is less soluble in the solution than zinc sulfide and so on, but experimental proof of this principle, which alone could decide whether the action were purely chemical, has not been advanced. Secondly, concerning the mode of action of the xanthate, it has generally been found that contact with air becomes possible at about the concentrations of metal and xanthate ions at which a precipitate of the metal xanthate forms. This is illustrated by the use of zinc sulfate to activate sphalerite. This type of evidence, which could be added to from the works of other writers, constitutes the case for the theory. Let us consider the case against it. Firstly, objections based on experimental evidence will be considered; secondly, certain theoretical objects will be discussed.

1. Some work on calcium heptoate has been cited by Gaudin and Hansen (6), which at first sight seems to support the theory. They deduce, "When the solution is saturated (with calcium heptoate) the superficial film of calcium soap (heptoate) is complete. At a concentration less than saturated, the superficial film is incomplete." A truly chemical theory implies *no* adsorption until the solution is saturated, and therefore the data may be used as an argument against the theory.

(2) It has not been shown decisively that contract first occurs under *exactly* the same conditions as precipitation. It would be difficult to prove this with the xanthates, because of their low solubility, but Gaudin's case of flotation of calcite by heptoic acid appears to be suitable for the test. Unfortunately, as pointed out above, this case does not indicate exact coincidence of these two conditions. Taggart and his collaborators have evidently noticed some similar flaws in the theory.

(3) Some unpublished work dealing with the effect of cyanide and alkali on adsorption of xanthates has shown that in many cases adsorption occurs under conditions where no heavy metal xanthate precipitation has occurred and that in others, despite the precipitation of xanthates, no adsorption of xanthate has occurred.

On theoretical grounds two difficulties arise. Firstly, it follows from the constancy of the angle for ethyl xanthate for different minerals (1), that the number of alkyl groups in the surface is independent of the mineral. The size of this group, rather than any dimensions of the crystal lattice, evidently determines the extent of adsorption. Therefore, every metallic and/or sulfide group of the surface may not be involved in anchoring the adsorption complex. Though (if this solubility or chemical theory is to hold) each xanthate ion takes the place of a sulfide ion in the surface, not every sulfide ion can be so replaced. The fate of those not replaced is uncertain. Do they pass into solution or is the final condition a mixed xanthate/sulfide surface with the xanthate portions shielding the sulfide? The solubility theory deals only with the possibility of and not with the extent of adsorption.

Secondly, the xanthates are stated by Weinig and Palmer (7) to be more soluble than the corresponding sulfides. The replacement of the sulfides of the surface by xanthates therefore needs further explanation. Taggart, Taylor, and Ince (8) and Taggart (9) have assumed that sulfides change on the surface to more soluble thiosulfates, sulfates, carbonates, hydroxides, etc.

The surface of galena can under certain conditions be changed to sulfate. Evidence has been adduced which shows that sulfate may be detected in solution after flotation of galena by xanthate. This evidence does not show, however, whether this sulfate is first formed at the surface and then replaced by xanthate, or whether it is formed by oxidation of sulfide ions which dissolve in the solution or which enter it as the result of metathesis with the xanthate. It would seem impossible to devise experiments to distinguish between these possibilities. It is perhaps significant that anglesite (natural lead sulfate) is more difficult to float than galena.

Accurate solubility determinations of xanthates and sulfides might prove it unnecessary, however, to assume the formation of any oxidized compounds on the surface. Even though the xanthate were more soluble than the sulfide, it is conceivable that the relatively high xanthate ion concentration might displace the equilibrium

$$PbS + 2X^- = PbX_2 + S^{--}$$

sufficiently to the right to allow the formation of lead xanthate on the surface.

The adsorption of xanthates by the noble metals (see following paper) can hardly be explained by metathesis. Excluding the doubtful possibility of surface oxidation, it must be concluded that xanthate ion or xanthic acid is directly adsorbed. Such a conclusion is at variance with the solubility or chemical theory of adsorption.

The balance of the evidence appears to be against the chemical theory, and for the present it is suggested that in its place there should be substituted the generalization, "The ability of a mineral to adsorb a soluble chemical flotation collector containing sulfur is closely related to the solubility of the salt formed by the collector and the metal of the mineral."

Concerning the second question, the time required after the mineral is placed in a xanthate solution before contact with air can be effected, was discussed very briefly in the paper previously mentioned (1). This discussion was concerned mainly with the development of the full equilibrium angle. Flotation, however, is possible, provided that an angle is possible—not necessarily the equilibrium angle—and it is therefore desirable to consider the speed with which sufficient adsorption occurs to enable any contact to occur.

Using any of the common sulfide minerals except galena, if contact is going to take place it is usually possible as soon as the bubble can be brought into contact with its surface after its immersion in the xanthate solution (25 mg. per liter). Even where activation is necessary, e.g., where sphalerite must be activated by copper sulfate, response is equally rapid. With lower xanthate concentrations adsorption may be a little slower, but generally, if contact is going to be possible, there is some indication of it within a minute or two. Other collectors (see the following paper) are adsorbed just as quickly.

Using galena, a second reaction apparently is possible which may interfere with the standard method used by us of detecting an adsorbed xanthate film. The nature of this reaction is at present unknown. It is prevented or removed by violent agitation of the test specimen with fine particles of galena or sand, such as would normally occur in a flotation machine. It is removed also by wiping the surface with a pad of linen, a process more easily carried out than agitation in a miniature flotation machine. It is now customary to wipe the surfaces of all minerals with linen prior to making the final measurements of contact angle. Generally, this is without effect on the angle, but occasionally, as in this case, or where a fine precipitate has settled on the surface, it is essential. Wiping the surface in this way does not remove the xanthate film. It is surmised that, where it is effective, the pad of linen removes an irregular film of some precipitate which has formed or settled on the surface and which mechanically prevents contact between the bubble and the adsorbed film on the surface.

With these precautions a chalcopyrite surface responds *fully* to 1 mg. per liter of potassium ethyl xanthate within five minutes and a galena surface within ten minutes.

Comparatively little attention has been paid in this laboratory to measurements of the rates of adsorption of xanthates by mineral surfaces. Arising out of earlier work the conviction has grown that an ideal flotation process must be based upon conditions where only one of the minerals to be separated is responsive to air, the other being completely non-responsive. Processes based upon differences in the rate of adsorption of xanthate have not appeared attractive.

The third question—the relationship between the angle of contact and the constitution of the collector—has been discussed in the paper already referred to (1). It is considered in greater detail in the next paper.

We wish to thank Mr. H. Hey for his constructive criticism in the preparation of this paper.

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THE PHYSICAL CHEMISTRY OF FLOTATION. III

The Relationship between Contact Angle and the Constitution of the Collector[1]

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Wark and Cox (1) demonstrated that the contact between air and mineral induced by potassium ethyl xanthate led to the development of a contact angle which was independent of the nature of the adsorbing solid and of the concentration of the xanthate; that another compound containing the ethoxy group, namely, sodium diethyl dithiophosphate, led to the same angle; that in the homologous series each xanthate led to a different angle, the size of the angle increasing with the number of carbon atoms in the alkyl group; and that several compounds containing substituted phenyl groups led to a substantially common angle. It was concluded that unimolecular films of these compounds were adsorbed at the surface of the adsorbing solid; that the collector molecules were orientated in such a way that the alkyl or aryl group was outermost and that they were packed as closely as the superficial area of the molecule would permit. It was also suspected that the non-polar group would prove to be entirely responsible for the magnitude of the angle of contact. The data of the present paper support these conclusions. They are also consistent with the theory that there is a close connection—not necessarily an identity—between adsorption of a collector and insolubility of its heavy metal salts.

It is to be emphasized that only sulfur-bearing compounds have been tested, and until other types of compounds have been investigated there must remain some uncertainty whether the angle of contact is completely independent of the polar group of the collector, to which, however, must be attributed its adsorption. Table 1 summarizes the results obtained to date. The blanks indicate that no measurements were made.

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[1] This work was done during the tenure of a Bartlett Research Scholarship at the Melbourne University, held by one of the authors (E. E. W.). It arose from observations made in the Flotation Research Laboratory of the University of Melbourne. This laboratory is maintained by a group of six mining companies, namely, the Broken Hill South Ltd., North Broken Hill Ltd., Zinc Corporation Ltd., Electrolytic Zinc Company of Australasia Ltd., Mount Lyell Mining & Railway Company, and Burma Corporation Ltd., and the other author (I. W. W.) is directly employed by these companies.

TABLE 1

Dependence of angle of contact on nature of adsorbed compound

(Abridged summary*)

ORGANIC TYPE	SPECIFIC NON-POLAR GROUP					
	Methyl	Ethyl	Butyl	Benzyl	Phenyl	Other cyclic derivatives
Disubstituted dithiocarbamate	50	60	—	—	—	68
Mercaptan	—	60	74	71	70	69 to 71
Xanthate†	50	60	74	72	—	71 to 75
Dithiophosphate	—	59	—	—	—	—
Trithiocarbonate	—	61	74	—	—	—
Monothiocarbonate	—	61	73	—	—	—

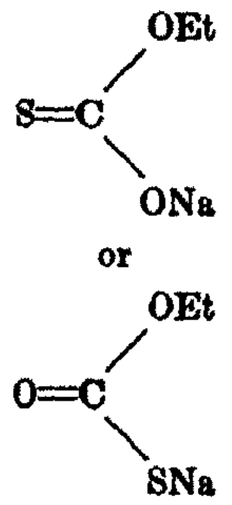
* This summary does not include the results for several non-polar groups which were investigated in one compound only. These follow in later tables.

† The results for the xanthates and for diethyl dithiophosphate are taken from the paper by Wark and Cox (1).

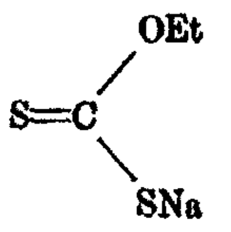
The following ethyl derivatives having thus given identical angles, it may be concluded that the number of ethyl groups in the compound influences neither the angle of contact nor the packing of the surface groups.

H—S—Et

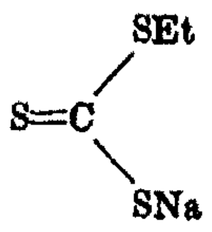
Mercaptan



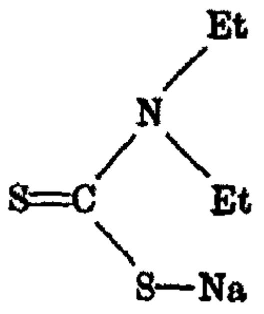
Monothiocarbonate



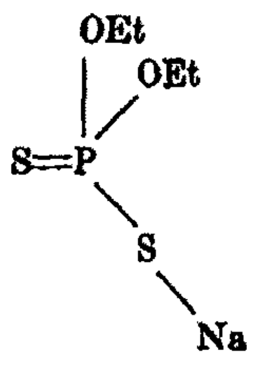
Dithiocarbonate



Trithiocarbonate



Dithiocarbamate



Dithiophosphate

It is of interest to compare the angle of contact at a unimolecular film with that at the surface of a solid containing the same surface group.

Unimolecular film of thiophenol	70°
Solid diphenyl surface	81 to 87°
Solid diphenyl ether surface	approximately 90°

The unimolecular film is evidently more polar than the solid compound.

EXPERIMENTAL METHOD

The method of measurement of contact angle has been described in detail by Wark and Cox (1). It is based on the method of Taggart, Taylor, and Ince (2), the important innovation being in the preparation of the mineral specimen by polishing. Polishing gives a reproducible surface at which the hysteresis is a minimum. A test of cleanliness is available, viz., that an air bubble will not make contact with a "clean" surface of any of the common sulfide minerals, of the metals, or of the common gangue minerals.

Briefly, the method of experiment is as follows: An air–mineral–water contact is effected at a horizontal surface by bringing a small bubble of air downwards into contact with the surface of a submerged mineral or metal specimen. A magnified image of the contact is projected on to a ground glass plate on which the angle of contact is easily measured. It is necessary to tap the support lightly to overcome the hysteresis effect. Recorded angles are the mean of at least six measurements. Duplicates agreed within 2°.

EXPERIMENTAL RESULTS

A. Adsorption of dithiocarbamates

The ammonium salts of the dithiocarbamates crystallize at room temperature from a mixture of the corresponding amine, carbon bisulfide, and ammonia. After extraction with acetone the product is sufficiently pure for testing; attempts at recrystallization generally lead to decomposition.

Table 2 presents the results for the compounds of this type. In many cases a mineral fails to respond to the compound unless "activated" by a heavy metal salt. Wark and Cox showed that sometimes the addition of a salt of the metal whose sulfide is being tested is sufficient to effect activation, but more often it is necessary to add the salt of a metal forming a less soluble sulfide. In the table, cases where activation is necessary are marked (a) or (b) respectively, corresponding to those two modes of activation. The symbol (p) signifies that the angle of contact was determined in a solution containing pyrogallol, which inhibits the formation of interfering oxidation products in the manner described later.

No attempt was made to determine the minimum effective concentration of any of the reagents employed; the aim was to determine the equilibrium contact angle under such conditions that contact was possible.

When using the diethyl dithiocarbamate, 25 mg. per liter of the salt generally sufficed. There was difficulty, however, in effecting contact at a pyrite surface, owing to very rapid fouling by the iron salt; this is formed because of the rapid rate of solution of the mineral.

Corresponding to the relatively high solubility of the heavy metal salts of dimethyl dithiocarbamic acid, high concentrations of the ammonium salt were necessary to induce adsorption. A 1 g. per liter solution was used throughout. Even with this concentration and using 10 mg. per liter of the specified activating agent, the full angle of contact developed only slowly for pyrite, galena, and sphalerite, but some contact occurred within an hour. Chalcopyrite responded fully within an hour. Failure to obtain a satisfactory angle for bornite was due to the surface becoming fouled by a precipitate of the copper salt.

TABLE 2

Contact angles at mineral surfaces in the presence of dithiocarbamate

MINERAL	DITHIOCARBAMATE					PIPERIDINIUM PIPERIDYL DITHIOFORMATE	DIMETHYL-DIPHENYL-THIURAM DISULFIDE
	Dimethyl	Diethyl	Monophenyl	Phenylmethyl	Phenylethyl		
Galena	50 (a)	59	54	50	61	70 (a)	50
Sphalerite	50 (b)	59 (b) 59 (b)	55 (b) 52 (b)	50 (b)	61 (b) 60 (a)	67	50 (b)
Pyrite	50	58	54 (p)	50	61	70	50
Chalcopyrite	50	59	—	49 (p)	62	67	50
Bornite	Irregular	62	54	50 (p)	62	67	50
Average	50	60	54	50	61	68	50

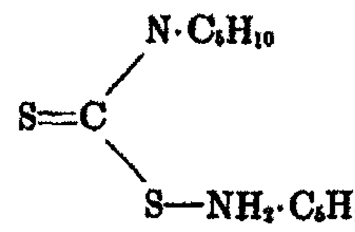
A higher concentration (a 1 g. per liter solution was used throughout) was also necessary with the methylphenyl compound, but the reaction was more rapid than with the dimethyl compound, 30 minutes usually sufficing for the maximum angle to be reached. Sphalerite, activated by 10 mg. per liter of silver sulfate, gave the customary methyl angle of 50°, but sphalerite, activated by 10 mg. per liter of cupric sulfate hydrate, and also the copper minerals gave a higher contact angle, 65°. This was attributed to the formation of a compound analogous to dixanthogen. Wark and Cox (1) have shown that dixanthogen, when present in the form of an emulsion which "oiled" the surface, gives a higher angle than xanthate. Dixanthogen tends to form spontaneously in xanthate solutions of this strength and it is probable that its analogue forms in dithiocarbamate solutions.

In further tests on the copper minerals, oxidation was prevented by the addition of pyrogallol (5 g. per liter). The normal angle was then obtained.

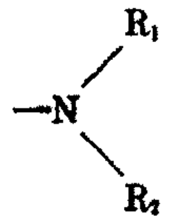
Twenty-five hundredths of a gram per liter of sodium sulfite was equally effective. Independent tests demonstrated that pyrogallol and sodium sulfite were without influence on the contact angle in normal cases and that they prevented the formation of dixanthogen under conditions where it would normally be slowly formed.

The corresponding dithiocarbamate oxidation product, namely, dimethyldiphenylthiuram disulfide was prepared. The response to this compound is rapid and a concentration as low as 15 mg. per liter is effective. Being a solid, it cannot oil the surface. It is not surprising, therefore, that it led to the same angle as the simple dithiocarbamate, but this leaves us at a loss to account for the high angle shown by the copper minerals in the absence of reducing agents.

Piperidinium piperidyl dithioformate,



is a member of the dithiocarbamate series. It has a closed ring in place of two alkyl groups



The piperidinium salt is obtained more easily than the ammonium, but both would ionize and their absorption reactions would be identical. It is surprising that the angle corresponding to this compound, 67 to 70°, is not closer to that for cyclohexanyl xanthate, 75°, but this indicates that the *whole* of the outermost group must be considered in predicting the contact angle. As the surfaces of the minerals were fouled very rapidly by precipitation of the heavy metal dithioformate, the maximum angle of contact was obtained only after wiping them free from precipitate with a small pad of linen.[2]

No abnormalities were observed with the phenylethyl compound except a tendency for bornite to give an angle slightly above normal, viz. 66°. This was not apparent in the presence of pyrogallol.

The results for the phenylethyl and diethyl compounds are identical. This may mean that in the former only ethyl groups are in the surface. Likewise the methylphenyl and dimethyl compounds yield identical angles.

[2] Angles are checked in this manner as a matter of routine; usually the wiping leaves the angle unaffected, but occasionally, as in this case, it is essential. Wiping in this manner corresponds to the agitation of the pulp in a flotation machine.

Though the angle for the phenyl group is 70°, monophenyl dithiocarbamate gives only 54°. It must be concluded therefore that both the hydrogen atom and the phenyl group influence the contact angle.[3]

Unsubstituted dithiocarbamate.—Ammonium dithoicarbamate, tried in various concentrations and with various activators, gives no reaction with pyrite or chalcopyrite. The concentrations employed were sufficient to give precipitates of iron and copper dithiocarbamate and if, as seems reasonable, it be concluded that the compound was absorbed, the unsubstituted amino group must give a zero angle of contact, i.e., it must be too polar for air attachment.

TABLE 3

Contact angles at mineral surfaces in the presence of mercaptans

MINERAL	ETHYL MERCAPTAN 500 mg. per liter	n-BUTYL MERCAPTAN	BENZYL MERCAPTAN	THIOPHENOL	THIOCRESOL	THIO-β-NAPHTHOL
Galena	0	73	71	68	71 68 (p)	70
Sphalerite	62 (b)	74	70 (b) 72	71 (b)	70 (b)	70
Pyrrhotite	—	—	—	71	—	—
Pyrite	57	74 (p)	69 (p)	71	72	68
Chalcopyrite	62	74 (p)	72 (p)	71	70	70
Bornite	—	—	72 (p)	—	71 (p)	—
Chalcocite	—	—	—	—	71 71 (p)	—
Covellite	—	—	—	—	72	—
Average	60	74	71	70	71	69

B. *Adsorption of mercaptans*

The compounds used were the purest available commmercially. It is known, however, that the mercaptans tend to oxidize spontaneously, the corresponding disulfides being formed. Oxidation would be helped by the presence of cupric and/or ferric ions. Consequently it was anticipated that, in testing the mercaptans, trouble would be experienced of a kind similar to that previously encountered with some xanthates. Such was indeed the case, abnormally high angles having been obtained in the following cases: thiocresol with bornite, benzyl mercaptan with all the copper and iron minerals, butyl mercaptan with pyrite and chalcopyrite (see

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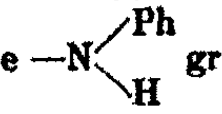
[3] This same angle has been obtained at the surface of certain copper minerals in the presence of thiocarbanilide. Both compounds contain the  $-\mathrm{N}\!<^{\mathrm{Ph}}_{\mathrm{H}}$ group.

table 3). The addition of pyrogallol (in these cases 5 g. per liter was used) was again effective in overcoming this difficulty.

Ethyl mercaptan and its heavy metal salts are relatively soluble in water. The customary 25 mg. per liter solution is not effective, but a 500 mg. per liter solution proved satisfactory for chalcopyrite, pyrite, and for sphalerite activated by 10 mg. per liter of silver sulfate. No contact was obtained with galena using 500 mg. per liter of the reagent, even in the presence of 25 mg. per liter of lead acetate. Activators of type (b) would probably have been effective. Higher concentrations than 25 mg. per liter of *n*-butyl mercaptan were also necessary; 500 mg. per liter sufficed for chalcopyrite and pyrite and 1 g. per liter for galena and sphalerite. A saturated solution of cetyl mercaptan failed to cause contact between the mineral surfaces and air. This may have been due to the very low solubility of the compound. Saturated solutions of thiocresol and thio-β-naphthol were used; these contain less than 25 mg. per liter. With benzyl mercaptan and thiophenol 25 mg. per liter solutions were employed.

TABLE 4

Contact angles at mineral surfaces in the presence of xanthates

MINERAL	*n*-OCTYL XANTHATE	SECONDARY OCTYL (CAPRYL) XANTHATE
Galena	85	90
Sphalerite	87 (b)	90 (b)
Pyrrhotite	85	90
Pyrite	86	90
Bornite	85	92
Average	86°	90°

C. Adsorption of xanthates

The adsorption of a number of xanthates was described by Wark and Cox (1). Only two additional xanthates have been prepared and tested, viz., *n*-octyl and *secondary* octyl. The results for these two compounds are in table 4. Sphalerite responds without activation but the full angle of contact is attained very slowly.

D. Adsorption of diethyl dithiophosphoric acid

Table 5 shows the results for the sodium diethyl dithiophosphate, which was obtained by courtesy of the American Cyanamid Company, which markets it under the trade name "Sodium Aerofloat."

Sodium diethyl dithiophosphate is more soluble than the corresponding xanthate; activation is therefore necessary for a greater number of the minerals. An angle of 80° sometimes develops; this is probably due to an oxidation product.

E. Adsorption of trithiocarbonates

The potassium salts of the trithiocarbonates crystallize from ice-cooled mixtures of potassium hydroxide, carbon bisulfide, and the corresponding mercaptans. They were recrystallized from a mixture of ether and benzene. Table 6 gives the results for the compounds of this type. Twenty-five milligrams per liter of trithiocarbonate was used throughout.

TABLE 5

Contact angles at mineral surfaces in the presence of sodium diethyl dithiophosphate

MINERAL	SODIUM DIETHYL DITHIOPHOSPHATE
Galena	58 (b)
Sphalerite	59 (b)
Pyrrhotite	59 (b)
Pyrite	59 (b)
Chalcopyrite	60
Chalcocite	60
Average	59

TABLE 6

Contact angles at mineral surfaces in the presence of trithiocarbonates

MINERAL	TRITHIOCARBONATE	
	Ethyl	Butyl
Galena	61	73
Sphalerite	60 (p) (b)	73
Bornite	60 (p)	74 (p)
Chalcopyrite	61 (p)	74 (p)
Pyrite	61 (p)	74 (p)
Average	61	74

F. Adsorption of monothiocarbonates

The potassium monothiocarbonates were prepared by passing carbonyl sulfide, generated from sodium thiocyanate and a 50 per cent aqueous solution of sulfuric acid, into a solution of potassium hydroxide in the corresponding alcohol. They were recrystallized from alcohol and washed with ether. Table 7 gives the results for these compounds.

The heavy metal salts of ethyl monothiocarbonic acid are relatively soluble. Chalcopyrite gives the full angle at a concentration of 25 mg. per liter, but with activated sphalerite 300 mg. per liter was necessary. Galena and pyrite gave no reaction with either 25 mg. per liter or 500 mg. per liter, but would no doubt respond to activators of type (b). The butyl monothiocarbonates are also too soluble for immediate or complete response to 25 mg. per liter of the potassium salt except in the case of bornite. The full angle, however, develops slowly without activators for all the minerals except sphalerite, and more rapidly with higher concentrations of the collector or with activators present. Galena evidently requires an activator to give the equilibrium value as the angle was somewhat low after five hours.

TABLE 7

Contact angles at mineral surfaces in the presence of monothiocarbonates

MINERAL	MONOTHIOCARBONATE	
	Ethyl	Butyl
Galena	0	(69)
Pyrite	0	72
Chalcopyrite	61	74
Sphalerite	61 (b)	72 (b)
Bornite	—	74
Average	61	73

TABLE 8

Angle of contact at metal surfaces in the presence of ethyl xanthate

METAL	ANGLE OF CONTACT	NOTES
Gold	61	
Silver	60 (p)	
Platinum	58	
Copper	60 (p)	
Tin	61	Polished on lead
Bismuth	61	
Antimony	58	
Arsenic	60	
Selenium	60	
Cadmium	60	Polished on lead
Zinc	Nil	Does not respond to activation by copper or silver salts
Iron	Nil	The surface fouls with extreme rapidity
Lead	Irregular	Surface produced by cutting; the surface became fouled too rapidly for satisfactory measurement.
Average	60°	

The solubility of the heavy metal salts of the thiosubstituted carbonates is, in order of decreasing solubility:—monothiocarbonates, dithiocarbonates, trithiocarbonates. The readiness with which they are adsorbed by minerals increases in this order.

G. Adsorption of ethyl xanthate at metal surfaces

The metal surfaces were prepared and tested in the same manner as the sulfide minerals. A 52 mg. per liter solution of potassium xanthate was used. Table 8 gives the results for the metals tested. The failure of zinc and iron to respond may be due to too great reactivity of the surface with water.

SUMMARY

The angles of contact due to several different types of flotation "collectors" have been investigated. The types investigated were xanthate, mercaptan, dithiocarbamate, dithiophosphate, trithiocarbonate, and monothiocarbonate.

It has been demonstrated that, when contact occurs, the angle at the line of triple contact air–solid–solution is dependent only upon the non-polar group of the adsorbed "collector." It is independent of the nature of the solid, of the polar or anchoring group of the collector, and of the concentration of the collector.

Whether adsorption of the collector occurs at a mineral or metal surface is related to the solubility of the corresponding metal salt of the collector.

We wish to record our thanks to Professor E. J. Hartung for having made available a laboratory for carrying out our research, and to Messrs. H. Hey and A. B. Cox for their help and criticism.

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THE PHYSICAL CHEMISTRY OF FLOTATION. IV

A Criticism of Ostwald's Theory of Flotation

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Wo. Ostwald (1) has advanced a theory of the action of soluble collectors, an essential part of which is that only a ring of the collector is necessary for flotation, the location of the ring being the air–water–mineral line of contact. The process by which this ring is assumed to be held is styled by him "adlineation." This theory is in opposition to that adopted by us (2), namely, that for soluble collectors a substantially complete unimolecular film is adsorbed by the surface of the mineral, and that for oleaginous collectors a continuous thin film spreads over the surface. The only evidence advanced by Ostwald in direct opposition to this view is a statement based on an observation of Kellermann (3) that the amount of added reagents is insufficient to form such a unimolecular film. This evidence has been questioned by Siedler, Moeller, and Reddehase (4), who cite work by Gaudin, Glover, Hansen, and Orr (5) which demonstrates that the amount of collectors used in practice is of the order required to form a unimolecular film over the surface of the mineral floated. Ostwald, in reply, questions the assumptions upon which Gaudin's and Siedler's calculations are based, but does not offer any further substantiation for Kellermann's views, and, in fact, admits the impossibility of determining accurately the number of molecules adsorbed per unit area of the mineral surface, except by a complete adsorption analysis.

In our opinion, it has not been proved that in any single case the number of effective collector molecules (certain frothers are also collectors) is insufficient to form a unimolecular film, but, apart from this, there is so much evidence against Ostwald's "adlineation" theory that even if, as seems unlikely, it were proved that Kellermann's view is correct, some explanation other than Ostwald's must be sought. Though finality has not been reached in deciding between the views of Kellermann and Gaudin, it is certain that in practice quantities of reagents must be added enormously in excess of those required to give an "adlineation" ring, and as it is impossible with the available technique to determine what fraction of these reagents is consumed by the minerals floated, any direct proof or disproof along these lines is impossible.

Indirect methods must therefore be adopted in determining whether the theory possesses the essential desiderata of a useful working theory. A theory need not be true to be useful, but to be useful a new theory should be simpler and more comprehensive than previous theories, and it should be in accord with known facts. Being an extreme development of the unimolecular film theory, Ostwald's theory cannot claim greater simplicity than it, and, not being applicable for insoluble collectors, it is not as comprehensive as the theory of complete filming. More important, the "adlineation" theory is not in accord with several experimental facts and accredited principles of surface physics.

Considering the turbulent conditions of the flotation pulp it is doubtful whether a ring of collector of the type suggested by Ostwald could lead to a sufficiently stable contact between air and mineral. Only if the ring acted as a perfectly mobile barrier could the air–mineral aggregates withstand the sudden stresses imposed upon them. Ostwald, in his second paper, attempts to show how the "adlineation" ring possesses this necessary mobility. Great mobility, however, could arise only from one of two causes. Firstly, the line of collector might be so loosely bound to the surface that free motion could occur. Actually xanthate films, far from being loosely held, are held by the surface with great tenacity. For example, chalcopyrite retains a xanthate coating after being washed for several minutes in running water, as is shown by the contact angle remaining the same as in a xanthate solution. Such tenacious adsorption is of considerable importance, since the xanthate film is the link which holds the mineral to the bubble. Secondly, great mobility might be due to the ring of the collector being securely bound to certain atoms of the crystal lattice which themselves possessed great mobility in the surface. Though this type of mobility is assumed for liquid films, we know of no evidence suggesting sufficient mobility of the atoms of a solid. Indeed Adam (6) states: "As a general rule, spreading on solids only occurs through the vapour . . . .; if the liquid is non-volatile, no spreading occurs, at least in any reasonable time." Adam's reference was to solids in contact with the atmosphere, but the generalization may apparently be extended to include contact with a liquid phase, in which case spreading only occurs through solution. Our experience would support such an extension, for the methods of experiment adopted in this laboratory would not have been possible had adsorbed films possessed appreciable mobility. Only one side of our test specimens of mineral is protected from contamination, and it is known that at least portions of the other sides are contaminated by grease and/or air, but experiment has shown that the area of contamination does not spread to the test face.

Perhaps the most convincing argument against great mobility is the phenomenon known as hysteresis. Several observers (7) have noticed that the air–mineral–water boundary is not perfectly mobile. The imperfect mobility is responsible for a difference between the angles of contact when water is replacing air and when air is replacing water at the mineral surface. The difference between these two angles has been called the hysteresis; it is due to friction.

The existence of a definite contact angle at the line of triple contact between air, water, and mineral has been accepted by Ostwald. It is universally accepted that if T_{as}, T_{wa}, and T_{sw} signify the surface energies at the air–solid, water–air, and solid–water interfaces, respectively, the magnitude of the angle of contact θ is determined by the relationship,

$$\cos \theta = \frac{T_{as} - T_{sw}}{T_{wa}}$$

DeWitt, Roper, and Makens (8) have shown that the magnitude of T_{wa} is practically unaltered by common collectors and frothers at the concentrations customarily employed. If, as Ostwald suggests, there is but a ring of collector at the line of triple contact, the air–solid and solid–water interfaces on either side of this line cannot be influenced by the collector, and the magnitudes of their interfacial energies would be identical with the corresponding values in pure water. Thus, if the "adlineation" theory were correct, the angle of contact would be independent both of the addition of a collector and of its nature. This is contrary to experience. At clean surfaces of many of the common minerals the angle of contact in pure water is zero, and if a collector be added the resultant finite angle varies with the nature of the essential non-polar radical of the collector (2).

Ostwald repeatedly stresses a generalization of Mayer that only unwettable particles float. We will return to a more exact statement of this principle later, but far from agreeing better, as Ostwald suggests, with his own theory than with other theories, Mayer's generalization is quite incompatible with Ostwald's theory, for it is only after the surfaces of the sulfide minerals have been changed by the collector that they become "unwettable." Furthermore, experiment shows that the whole of a collector-conditioned mineral surface is actually different from a surface which has had no contact with collector; the change is not confined to a single line on the surface or to any small fraction of the surface. For if the specimen be washed and placed in distilled water a bubble of air will effect contact with any part of the surface even though the surface be "swept" several times by air bubbles.

It is well to consider what is meant by the term "unwettable." Ostwald cites Edser (7) as stating that in no known case does the angle of contact at the air–water–solid boundary reach 180°. This implies that when contact with air is possible, equilibrium can be established with a portion of the solid surface in contact with air and a portion with water, the air-water interface being inclined at an angle to the solid suface. The extent of the displacement of the water from the surface depends upon the volume of the air, the angle of contact, and the size and shape of the surface of the particle. The term "unwettable" is, therefore, misleading, and we suggest in place of Mayer's generalization the statement, "No particle will float at an air-water interface unless both air and water are in contact with its surface, that is, unless there is a finite contact angle at a line of triple contact between air, solid, and water."

At surfaces of substances such as diphenyl and paraffin wax, water is readily displaced by air, the equilibrium contact angles being approximately 84° and 105°, respectively, for the above two substances. Bubbles of air will readily attach themselves to such solids, and particles of diphenyl (sp. gr. = 1.16) may be floated readily to the surface of water. There is, moreover, no visible difference between the type of contact of an air bubble with diphenyl and with a mineral surface which has been in contact with a soluble collector, nor in the type of flotation. Since the surface of diphenyl must consist exclusively of hydrocarbon groups, there is no possibility of the presence of a mobile triphilic[1] ring at the line of triple contact. Ostwald's theory, therefore, cannot have universal application in accounting for the mechanism of flotation.

Indeed, Ostwald does not use the "adlineation" theory for oleaginous collectors. For these he makes use of a theory of "laminar" flotation. This theory was propounded in very similar terms by Christmann (9). The essential feature of the theory is that superimposed on the collector film at the mineral surface there is a second film composed of frother molecules and that the dual film is air-avid and induces flotation. Ostwald states that there must be an adherence between the collector and frother films, and Christmann that an orientated hydrocarbon film of collector is soluble in the hydrocarbon film of the frother. The orientation of the frother molecules necessary for these conditions to be fulfilled, however, would be such that the assumed dual film could not be air-avid. The collector is bound to the mineral surface by its active group, the non-polar group being orientated away from the mineral. The frother molecule, if it be soluble in this film as Christmann suggests, or if it adhere as Ostwald

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[1] Ostwald considers that soluble collectors must be of a triphilic nature, i.e., contain three groups of essentially different type, whose function is to stabilize the air-water-mineral contact, each group of the collector making contact with only one phase. Since the hydrocarbon groups in the surface of diphenyl can make contact with both air and water such an hypothesis is not essential to account for flotation. Moreover, it would require abandonment of the usual conceptions of atomic attractions to ascribe a triphilic nature to such soluble collectors as the quaternary ammonium salts and mercaptides.

suggests, must therefore be orientated with its non-polar group towards, and its polar or water-avid group away from the mineral. Therefore, the dually filmed particle could not float. Actually the orientation of the frother molecule at the air–water interface is such that its non-polar group is directed towards the air phase and the polar group towards the water phase; such orientation would oppose any adherence or mutual solubility of the collector and frother films.

It is our view that the essential function of the frother is to stabilize the large air–water interface necessary for froth flotation, which stabilization is undoubtedly achieved because of adsorption (either positive or negative) at this interface. During the process of formation of the air–mineral aggregate the frother is squeezed from the surface of the bubble, and air then makes direct contact with the air-avid collector film. This collector film on the mineral surface may be an orientated adsorbed unimolecular layer, as in the case of soluble collectors, or a more discrete film of an insoluble collector as in the case of oils. The difference between soluble and insoluble collectors does not therefore lead to a difference in the mechanism of formation and stabilization of air–mineral aggregates, but to a difference in the means by which they render a mineral surface air-avid. It is thus unnecessary to postulate a number of complex theories of flotation to cover the use of different types of collectors.

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COMMUNICATIONS TO THE EDITOR

THE THEORY OF THE STICK ANTIMONY ELECTRODE

The stick antimony electrode is a type of the metal-metal oxide electrode, the antimony oxide being present as an adsorbed film on the surface of the metal. This oxide is formed by air oxidation on the metal surface after polishing. The reaction of this adsorbed film with the hydrogen-ions in the solution sets up a potential, according to the reaction (Roberts and Fenwick: J. Am. Chem. Soc. **50,** 2125 (1928)):

$$Sb_2O_3 + 6H^+ + 6(-) = 2Sb^0 + 3H_2O$$

The potential is found by the Nernst equation:

$$E = E_c - \frac{RT}{6F} \ln \frac{(Sb_2O_3)(H^+)^6}{(Sb^0)^2(H_2O)^3}$$

Developing the equation:

$$E = E_c - \frac{RT}{6F} \ln (H^+)^6 = E_c - \frac{RT}{F} \ln (H^+) = E_c + 0.05915 \text{ pH}$$

This potential is identical with that developed from the solution of the metal forming its ions in a solution saturated with the metallic oxide.

However, it is not necessary for the solution being measured to be saturated with the insoluble oxide for the metal-metal oxide electrode to function correctly. Tartar and McClain (J. Am. Chem. Soc. **53,** 3201 (1931)) have stated that the potential of a metal electrode is due "to an adsorbed ionic film extending from the electrode a measurable distance out into the solution." Since this is so, an adsorbed oxide film on a metal electrode will furnish saturation of that portion of the solution from which the potential is derived. From this it would seem that the electrode reaction takes place at the interface of the metal with its oxide.

In preliminary work with several stick metal electrodes, as antimony, bismuth, tungsten and tantalum, the potential obtained seemed to be dependent on the nature, thickness and stability of the oxide film on the metal. The oxide should be a definite compound, not a mixture of oxides, and of specific crystalline form (Roberts and Fenwick: J. Am. Chem. Soc. **50,** 2125 (1928)). The thickness of the film should be such that it will allow penetration of the solution to the metal. A thick film of the oxide on a metallic stick tends to slip off, as a glove from the finger. This supports the contention that the electrode reaction takes place at the interface of a metal with its oxide. If the oxide film dissolves, ions will be formed in the solution which will affect the potential being measured. It would seem that any stable metal which could have an adsorbed film of its compound insoluble in the solution might function as a measure of the hydrogen-ion concentration of that solution.

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THE THEORETICAL LIMITATIONS OF THE STICK ANTIMONY ELECTRODE

In a recent paper (Parks and Beard: J. Am. Chem. Soc. **54**, 856 (1932)) the authors have shown that stick antimony electrodes in unstirred buffer solutions in contact with air may be calibrated to give a curve which agrees with that of the hydrogen electrode as to slope, thus satisfying the Nernst equation from the pH value of 1.60 to that of 7.87.

In a highly acid solution, pH lower than 1.60, the potentials obtained with the stick antimony electrode are not a true measure of the pH of the solution, because the adsorbed film of Sb_2O_3 on the metal electrode has dissolved and antimonyl ions have been formed according to the reaction

$$Sb_2O_3 + 2H^+ = 2SbO^+ + H_2O$$

Antimonyl ions with hydrogen-ions in equilibrium with the antimony metal and water develop a potential (Schuhmann: J. Am. Chem. Soc. **46**, 52 (1924)) which may be found by the Nernst equation:

$$E = E_0 - \frac{RT}{3F}\ln\frac{(SbO^+)(H^+)^2}{(Sb^0)(H_2O)} = E_0 - \frac{RT}{3F}\ln\,(SbO^+)(H^+)^2$$

Thus the concentration of the antimonyl ion is a factor in the potential developed and the electrode does not correctly measure the hydrogen-ion concentration of highly acid solutions.

In alkaline solutions, above pH 10.53, there is also a deviation of the values obtained by the stick antimony electrode away from the theoretical values. The deviation in this range is due to the antimonite ions (SbO_2^-) in the solution formed by the dissolving of the adsorbed film of antimony oxide on the metal stick by hydroxyl ions according to the reaction

$$Sb_2O_3 + 2OH^- = 2SbO_2^- + H_2O$$

These antimonite ions with water in equilibrium with the metal and hydroxyl ions give a potential (Grube and Schweigardt: Z. Elektrochem. **29**, 257 (1923)) which may be found by the Nernst equation:

$$E = E_0' - \frac{RT}{3F}\ln\frac{(SbO_2^-)(H_2O)^2}{(Sb^0)(OH^-)^4} = E_0 - \frac{RT}{3F}\ln\,(SbO_2^-)(H^+)^4$$

Thus in extreme alkaline solutions the potential will be that denoted by the Nernst equation involving the SbO_2^- ion, and does not give a value that is a measure of the hydrogen-ion concentration of the solution.

The deviation of the stick antimony electrode values between pH 7.87 and 10.53 away from the theoretical values is due to a differential effect of the Sb_2O_3 and the SbO_2^- ions. If the Sb_2O_3 alone were present with increasing pH (from 7.87) the curve would continue in a straight line from its lower values and give higher potentials. If, on the other hand, the SbO_2^- ion were the only antimony ion present with decreasing pH (from 10.53) lower potentials would be obtained according to the Nernst equation which has (SbO_2^-) as a factor. Grube and Schweigardt (Z. Elektrochem. **29**, 257 (1923)) state that the SbO^-_2 ion readily absorbs oxygen from the air. This excess oxygen in the solution in contact with the metal would aid in the formation of Sb_2O_3 and so retard the deviation of the values in this range.

Thus in extreme acid and alkaline solutions where there is a limited amount of antimony oxide, as in the case of an adsorbed film on a metallic stick, the potential obtained by the stick antimony electrode is not a true measure of the hydrogen-ion concentration of the solution due to the formation of oxy-antimony ions in the solution. Although the stick antimony electrode is very convenient as a means of measuring the hydrogen-ion concentration of a solution, it is theoretically correct only in the pH range from 1.60 to 7.87. In alkaline and highly acid solutions the electrode can be used only if it has been previously calibrated.

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THE RÔLE OF SURFACE ELECTRONS IN ADSORPTION AND CATALYSIS

A theory that the adsorption of gases by metals and the catalysis of reactions following this adsorption is due to some electrical or mechanical effect of the surface electrons of the metal was advanced by Pisarzhevskii (Ukrain. Khem. Zhur. **1**, 1–18 (1925)) in 1925. More recently this idea has been taken up again by Nyrop (Chemistry & Industry **50**, 752–5 (1931) and Phys. Rev. **39**, 967–76 (1932)), who gives it a more theoretical and mathematical treatment. A quotation from the abstract (C. A. **22**, 2512 (1928)) of the Pisarzhevskii paper will serve to give the nature of his theory: "Catalytic activity of metals is due to freely moving electrons. Adsorption of gases by metals is the result of electrostatic forces between gaseous mols. and a film of free electrons on the surface of metals. Impacts of these electrons on the adsorbed mols. produce their dissociation and ionization and cause thereby chem. reactions."

According to Nyrop, ionization of the gas molecules precedes adsorption and will occur in cases where the metal has free electrons of sufficient kinetic energy. Once adsorption has occurred, the possibility of reaction and the course of the reaction with some other gas that may be adsorbed depends on the energy required for ionization of the resulting substance and its rate of diffusion away from the metallic surface.

In connection with a general study of the mechanism of heterogeneous catalysis started some time ago in this laboratory, experiments to test this theory were performed. A nickel strip catalyst was used in the reaction of hydrogen and oxygen. Numerous runs were made with this catalyst supposedly activated by the impression on it of a high frequency electrical current. The following may be given as argument that during such a treatment the activity of the catalyst should be increased if the Pisarzhevskii-Nyrop theory is valid.

Increase in catalytic activity should result from (1) an increase in kinetic energy of the free surface electrons, and/or from (2) an increase in their concentration. With alternating currents of 5000 cycles, a "skin effect" is generally quite appreciable (Kennelly, Laws, and Pierce: J. Am. Inst. Elect. Engrs. **34**, 1953 (1915)) and with greater rapidity of alternation this effect becomes more pronounced. With the current and its attendant heat generation concentrated on the surface of the conductor, the kinetic energy of the electrons there becomes greater than is normal for the temperature of the metallic mass as a whole.

As to concentration of the free electrons (i.e., those electrons in a metallic conductor to which classical theory ascribes conductance) on the surface, it is only necessary to consider the probable change as the frequency of an alternating current of any given strength is made greater. As the current becomes more and more a phenomenon of the surface only, either the number of free electrons on the surface must increase or their mean free path must change in order to accommodate the higher current density. Either or both of the changes should make for more collisions with gas molecules and hence greater catalytic power.

Frequencies of about 50 kilocycles with currents up to 50 milliamperes were used in the experiments. In no case was there any evidence of increased catalytic activity.

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NEW BOOKS

Thermochemie. By **Dr. W. A. Roth.** 102 pp.; 15 figs. Sammlung Göschen. Berlin: Walter de Gruyter and Co., 1932. Price: RM. 1.62.

This small volume by a skilled experimenter in the field contains an excellent, condensed treatment of thermochemical practice. Students who desire to become acquainted with the best methods of attacking thermochemical problems will find this book of considerable value Even the experienced thermochemist will find many useful hints scattered through this volume. The author has included a short treatment of thermodynamics. Thermochemical data appear only as illustrative material.

F. H. MacDougall.

Dizinario di Chimica Generale e Industriale. Volume I, A–E. By **Prof. Michele Guia and Dr. Clara Giua-Lollini.** 29 x 20 cm.; ii + 1082 pp. Turin: Urime Tipografico-Editrice Torinese (Utet), 1933. Price: L. 165.

This is a formidable first volume of a Dictionary of Chemistry, concerned not only with the theoretical aspects of the science, but also with its varied application to agriculture, biology, pharmacy, geology, and mineralogy. The whole, when completed, will be no small achievement for only two authors. In view of the existence of other seemingly similar compilations, e.g., Thorpe or Ullmann, each the combined work of many specialists, the question may be asked, what is there to justify this new work, apart from its being Italian and up to date?

The answer is that it covers new ground. The information given under each heading is, in the main, comprehensive, without very great detail, and is in general stated so simply that anyone without special knowledge of chemistry can get valuable information from it. At the same time useful references are appended for anyone who requires more. The inclusion of short biographies of past chemists, from the earliest times, and technologists of later date, and the large part of the work devoted to chemical theory and pure science, differentiate it from the dictionaries or encyclopedias dealing only with applied or technical chemistry. Indeed another Italian compilation is probably the only one on similar lines, i.e., *Nuova Enciclopedia di Chimica,* founded by Guareschi and continued by others in thirteen volumes.

In the volume under review much is open to criticism, chiefly on the ground that subjects are inadequately dealt with. More modern work is often omitted, e.g., molecular association is chiefly devoted to the work of Ramsay and Shields, or under such headings as catalysis, etc. On the other hand, many good accounts are given, e.g., of the history of the atomic theory, crystal form, chemical affinity, etc.

On the technical side the detail given is not always distributed proportionately to the importance of the subject considered, but, as is to be expected, materials important to, or products of, Italian industry are exceptionally well done, e.g., boric acid.

This first volume contains twenty-eight tables and five hundred and sixty-five illustrations. Should the succeeding volumes maintain the high standard already achieved, the whole should prove a useful and necessary work of reference.

W. H. Patterson.

L'Azéotropisme. La tension de vapeur des mélanges de liquides. Bibliographie. By **Maurice Lecat.** 24.5 x 16 cm.; viii + 264 pp. (Printed on one side of the paper only). Brussels: Lamertin, 1932. Price: 15 belgas.

Azeotropy is a subject of increasing importance both in the research laboratory and in industry, and the determinations of the vapor pressures of mixed liquids have important theoretical implications at the moment. Professor Lecat has made an exhaustive study of the literature of azeotropism, and has himself examined over two thousand mixtures and discovered a great many azeotropic mixtures. Before the appearance of this volume the literature and details regarding the phenomena were collected by him in a volume published in 1918 having almost the same title as the book under review. The data in Professor Sidney Young's well-known book *Distillation Principles and Processes* (1922) and also in the *International Critical Tables*, Vol. III, p. 318 (1928), were based largely on this former volume, and we are referred to it in the Tables for further details and literature regarding the azeotropic systems there cited, each system being given a number termed Lecat's number.

The volume under review contains a list, in alphabetical order, of the authors of papers and other publications on azeotropism and the vapor pressures of liquid mixtures. The complete reference with the full title of the paper or book is given. A second more concise list arranges the works chronologically, and gives an abbreviated reference. A third list gives the journals and books, already quoted in the previous lists, in alphabetical order. Cross references are given in both of these to the first list. All the lists are printed on one side of the paper only. As is only to be expected in a work of this kind, there are a few omissions in the later years.

In the preface we are promised shortly another book entitled *Tables d'azéotropes binaires*, and it is probable that these tables will contain the azeotropic mixtures arranged by subject, and will therefore be a necessary companion volume to this one. Professor Lecat should have our thanks for having carried through an enormous task most successfully. It will be a welcome addition to the shelves of all chemical libraries.

D. C. JONES.

Third and Final Report of the Adhesives Research Committee. By the Adhesives Research Committee appointed by the Department of Scientific and Industrial Research. 24 x 15 cm.; v + 109 pp. London: H.M. Stationery Office, 1932. Price: 2/6.

The third and final report of the Adhesives Research Committee contains the report proper, together with three appendices. Appendix I describes the final stages of the work conducted by Mr. Douglas and Miss Pettifor at the Royal Aircraft Establishment on the mechanical testing of timber-glue joints. Appendix II reports further progress in the work conducted by the late Professor Schryver and his collaborators at the Imperial College of Science and Technology on the chemistry of gelatin. Appendix III describes further investigations into the nature of adhesion by Professor McBain, with Dr. Lee, at Bristol University, and later at Stanford University.

Most of the work described in the appendices has appeared already in various publications. The later stages of the research dealt with in Appendix I are given more fully here, and the conclusions of the authors as to the best type of test-piece, the most suitable timber, and the procedure best adapted for reducing in number the many experiments necessary to arrive at a representative value for a certain glue, are given with complete tabulated experimental results, and numerous illustrations.

Appendices II and III both contain discussions of work of great interest to chemists. Professor Schryver (with Dr. H. W. Buston) describes in a general way his work on the purification of gelatin, and gives a more detailed account, in chronological order, of the work done on the intramolecular changes that gelatin undergoes. A short section is devoted to the methods of protein analysis, but this part of the work remains incomplete. Appendix III is divided into six parts, the heads to which give a rough idea of the comprehensiveness of the treatment by Professor McBain. Part I is a general survey of the new results; Part II contains the work on pure chemical substances as adhesives; Part III deals with the adhesion of gums, resins, and waxes to metals; Part IV with the tensile strength of free films (thin strips) of adhesive; Part V with adhesion in glued wood joints; Part VI gives a very brief account of solvents and swelling agents for organophilic adhesives.

The work contained in both these appendices is left unfinished, owing in one case to the death of Professor Schryver, and in the other to the transference of Professor McBain to Stanford University. It is sincerely to be hoped that the work will be continued in some way. The problems of Appendix III, especially, involve for their complete solution apparatus and technique which usually can be obtained only in such laboratories as the National Physical or the Bureau of Standards. For example, one of the most interesting tentative conclusions, both from a theoretical and practical standpoint, is that "the thinner the film the stronger the joint"; but the methods of measuring the thicknesses of these films, of preparing the plane surfaces of the testing pieces, and of ensuring a complete film of adhesive, present problems of great technical difficulty.

This third report is an excellent testimonial to the value of the work sponsored by the Adhesives Research Committee.

D. C. JONES.

Periodisches System, Geschichte und Theorie. By E. RABINOWITSCH AND E. THILO. 302 pp.; 50 figs.; 49 tables. Stuttgart: Verlag von F. Enke, 1930.

The theory of atomic structure has reached in the researches of Bohr, Heisenberg, Pauli, Russel, Saunders, and Hund a certain stage of development which makes it profitable to review the fundamental principles of chemistry and to discuss the most important aspect of chemistry,—the periodic system of the elements. This task the authors set themselves in this volume, and be it said at once they have been eminently successful. Their discussions are very lucid and it is a pleasure to read their book. The reviewer enjoyed the examination of this treatise so much that he only regrets that the authors have been forced, probably on account of length of space available, to abbreviate the treatment of certain topics which it would have been a pleasure to see discussed in their vivid and logical style. However, the volume is intended to be a textbook rather than a complete treatise on the subject. Students who approach the topics discussed for the first time will find that every paragraph is of importance and in some instances they will have to supplement their reading by reference to other works or to the original literature. However no extensive literature references are given, although the names of investigators who have made important contributions to the modern study of atomic structure theory are mentioned throughout the text. The treatment is quite "non-mathematical" and for this reason some of the beauty of development and deduction is lost at times. The authors bravely attempt to discuss modern quantum theory on a minimum of mathematical treatment and they succeed remarkably well. However, it seems that a student desirous of a complete understanding of "wave mechanics" will be by necessity be forced to go into the mathematical treatment of the subject.

The book is divided into five parts. Part I, "History of the natural system of the elements," begins with a review of the philosophical ideas of the ancients and traces the development of the atomic theory and the progress made in the systematic study of the elements culminating in the periodic system as known today. Part II, "The building stones of the atoms," contains a brief discussion of the electrons, the proton and the atomic nuclei and atomic numbers. Part III, "The model of the atom," deals with the part spectroscopy has played in the development of modern notions of the atom. The treatment given modern spectroscopic theory is excellent. The arrangement of the spectrum lines into series, the simplification produced by the introduction of terms etc. are all dealt with in a satisfactory manner. The Bohr hydrogen atom model forms of course the background of the discussion. Its extension to many electron atoms, the shell model of the atoms, x-ray spectra, the empirical arrangement of terms, selection principles, the need for four quantum numbers for a complete description of the energy state of an electron, the Pauli principle, the formal model of an atom with several valency electrons and the wave mechanical model of the atom are developed in this section. Part III is the longest section (100 pages) of the book and contains material every chemist should be familiar with. The next portion of the book, (Part IV) "The development of the periodic system," shows the construction of the various elements as far as the arrangement of the electrons into various shells or states is concerned and it also gives the normal state of the element in the modern notation. Part V, "The periodicity of chemical properties," contains a discussion of chemical valency, ionic and atomic binding, the Haber-Born cycle, ionization potentials, electron-affinities, forces acting between ions, ionic radii, lattice energies, and Heitler-London theory of non-polar valency.

It is seen that only the simpler structures are treated. The coördination compounds, which form a very large class of substances, are not dealt with.

The systematic arrangement of the electron structures of the elements which is obtained from spectroscopic theory evidently appeals to the authors very much and the reviewer certainly shares their attitude. But in their enthusiasm they are willing to place helium in the periodic table (table 38) into the second group, because helium has the electron arrangement s^2, ^1S, which is also the arrangement for the valency shell of the alkaline earths! But the outer pair of electrons in the alkaline earths is held so much more loosely that these metals have nothing chemically in common with the rare gas-like helium! However, the reader of the book will certainly obtain a picture of the periodic table based on modern physical theory, and to chemists who wish to keep abreast of the modern development of the fundamentals of their science and to the younger generation who wishes to obtain this basic knowledge the book can be heartily recommended.

GEORGE GLOCKLER.

L'atomistica moderna e la chimica. By M. Haissinsky, edited by U. Hoepli. 307 pp. Milan, 1930. Preface by N. Parravano, Director of the Chemical Institute of the University of Rome.

The author covers the whole field of modern atomistics from the physical and chemical angles and necessarily he must be brief within the space of the book. The treatment is therefore most concise and whenever mathematical formulation is desirable or necessary he contents himself to state relations in mathematical terms without showing their derivation from more fundamental principles. It is really astonishing that he succeeds in covering such a multitude of topics in such limited space. But he certainly does succeed, and the book gives the Italian chemist a complete view of modern knowledge and theory of atomic structure and the bearing these notions have upon chemical principles.

The twelve chapters cover the following topics: I. Molecules, atoms, and electrons. II. Thermodynamics and quanta. III. The Atom of Bohr. IV. The electronic theory of valency. V. Born's theory of grating energy. VI. Applications of Born's theory. VII. Electric charge, atomic radii, and electronic structure. VIII. Deformation of electronic orbits. IX. Photochemistry. X. Photochemical theory. XI. Catalysis and adsorption. XII. Wave mechanics and Fermi statistics. But this résumé does not give even yet all of the material covered, for each chapter consists of many subdivisions, and it appears that no topic has been left unmentioned that may have some connection with modern atomic and molecular theory. However the Raman effect is not mentioned, although it was discovered in the year 1928.

Each chapter contains at the end a bibliography of the important articles, books, monographs, and treatises of the material covered in that chapter. An author index is appended but no subject index is included. However, the table of contents is very complete with many subdivisions and the reader should not have undue difficulty in locating a desired subject in the body of the book. While of course the same material is covered in many treatises, it will appeal to the American chemist of linguistic tendencies to study the topics involved in the Italian language.

GEORGE GLOCKLER.

Atom and Cosmos. By HANS REICHENBACH, translated by Edward S. Allen. New York: The MacMillan Company, 1933. Price: $2.00.

In our present state of turmoil in science, and in physics in particular—where discoveries quickly follow discoveries, new theories supersede each other in rapid succession, and contradictions are the order of the day—it is refreshing to find a book in which the fundamental conceptions at issue are so clearly discussed.

In as simple language as is consistent with such a difficult problem, Professor Reichenbach, who holds the chair of Natural Philosophy in the University of Berlin, gradually develops his subject, and shows, first, that it is not merely a "mania for speculation" nor a disagreement upon facts between different observers that has led to the present crisis. Its roots go far deeper, and what is at stake is no less than a revolution of our entire conception of the cosmos, involving a making over of philosophy, and a revolution as far reaching in its consequences as Copernicus' break from the Ptolemaic and Aristotelian doctrines.

First giving us an insight into the world of the astronomer, the world of space and time, and of great dimensions, then, with the aid of a ray of light and its electrical interpretations, leading us into the realm of atomic physics with its minute dimensions but immense forces, Professor Reichenbach, in a final summing-up, discusses the bearing of all this upon our philosophy of science. It is shown that ours is a world of mediocrity; that our "laws" of nature are laws only insofar as they apply to a world of moderate dimensions; that these laws which give us a semblance of certainty are in reality neither immutable nor even "true," but only practically so, by virtue of the fact that they represent statistical averages of a gigantic number of separate entities. In the microcosmos, the world of the atom, there are no such concepts as certainty or causality, while in the macrocosmos, in interstellar space, there is not that geometrical simplicity of Euclid which we formerly ascribed to it.

Perhaps one of the best features of the book is that the author develops his argument by actually following the line of reasoning of the physicist and the mathematician, and makes use only sparingly of that now so popular device of analogues, which, though unquestionably simpler and more gratifying to the uninitiated, is so often misleading as well.

As a guide into contemporary scientific philosophy this volume of Professor Reichenbach is one of the very best that has come to this reviewer's notice. The English translation by Professor Edward S. Allen of Iowa State College, maintains throughout a high degree of excellence. The only slip that I have been able to find is on p. 202, where reference is made to the *American* physicist, C. T. R. Wilson.

As stated in the preface the book is an outgrowth of a series of lectures broadcast by the author in Berlin during 1929–30. One must admire equally the skill with which Professor Reichenbach has adapted his presentation to such needs, and the courage of the broadcasting station in unleashing such material on the public, and wish that we could do the same with our enlightened populace.

W. J. LUYTEN.

Signals from the Stars. By George Ellery Hale. New York: Charles Scribner & Sons.

This little book, by Dr. Hale of the Mt. Wilson Observatory, is the fourth in a series of recent aspects and achievements in astronomy. It deals particularly with the possibilities of large telescopes and with the phenomena of the solar atmosphere.

Dr. Hale's own contribution to the science and the large share he has had in the planning and organizing of astronomical research accord him an undisputed authority in these fields; from his previous books the lucidity of his style is too well-known to need further comment.

An interesting dissertation on lenses precedes the discussion of giant modern telescopes; a chapter follows which deals especially with the observations of the sun's atmosphere and the correlation between solar and terrestrial magnetic phenomena. The last part of the book is devoted to a description of how the proposed 200-inch telescope might be built, and what it is hoped might be accomplished with it.

Not the least attractive part of the book is formed by the selection of photographs and illustrations. In particular this reviewer was struck by the remarkable photograph at the end which so clearly shows the distance effect in the recessional velocities of spiral nebulae.

W. J. Luyten.

Moderne Physik. Sieben Vorträge über Materie und Strahlung. By Max Born. 24 x 16 cm.; vii + 272 pp. Berlin: Julius Springer, 1933. Price: unbound, 18 RM.; bound, 19.50 RM.

In 1932 the Technische Hochschule of Berlin and the Elektrotechnische Verein, considering that the remarkable recent developments of physics were of great interest, and might be of great importance, to electrical engineers, decided to arrange a series of lectures which should describe these developments in a way generally intelligible to the technical men in question. They were fortunate enough to obtain Professor Born, of Göttingen, who is well-known to all English physicists and physical chemists for his work on the solid state and on the new quantum mechanics, as the expositor, and the book before us is based on the seven lectures which he gave, the matter of those lectures having been worked up and prepared for the press by Dr. Fritz Sauter.

Obvious difficulties of the task which Professor Born set himself are the selection of the matter and the rendering of it in a form understandable without profound mathematics, especially such developments as the principles of wave mechanics and the new types of quantum statistics known by the names of Bose-Einstein and Fermi-Dirac. The selection is very properly dictated by Professor Born's particular interests, but fortunately they cover the most important aspects of modern quantum theory, and there is a large and fashionable school which will maintain that, as the title of the book implies, this is all that matters in modern physics. The presentation is, considering the nature of the subjects, extremely clear and free from difficult mathematics, all detailed calculations being relegated to an appendix, where they are carried through with elegance and with freedom from the more troublesome mathematical technique.

It must not be understood that the book is altogether easy reading for a student without previous acquaintance with the subject, but it should present no insuperable difficulties to those who have a moderate knowledge of the old dynamical theory of gases, and have read some good general account of atomic structure. It is from the kinetic theory of gases that the author, naturally enough, sets out, laying stress on the nature of the assumptions. He then proceeds to deal with the elementary particles, and with the wave-corpuscle dilemma, dichotomy, duality—call it what you will. This leads on to the Bohr atom, and its insufficiencies, which the matrix mechanics and wave mechanics have, as briefly described, so substantially reduced. The explanation of doublets and other features of the spectrum by the spinning electron and Pauli's exclusion principle occupy the fifth chapter. The stage is then prepared for a discussion of the modern systems of statistics, with the difficult conception of a degenerate gas, which has proved so valuable for the theory of the conduction of electricity in metals, even if superconductivity still defies the theorists. This part of the book in particular reveals the master, the relation of the two new systems of statistics to one another and to the older Planck and Boltzmann statistics being exposed about as well as could possibly be done in so restricted a space. The final chapter contains a general discussion of the problem of chemical combination as seen by the modern physicist.

There is ample evidence of the care which Dr. Sauter has devoted to his task of revision. In short, the book gives a beautifully balanced summary of some of the most fascinating developments of modern theoretical physics.

E. N. DA C. ANDRADE.

Lipoide und Ionen. By DR. A. DEGKWITZ. 15.5 x 22 cm.; xvi + 323 pp. Dresden and Leipzig: Steinkopff, 1933. Price: bound, 29.20 M.; unbound, 28.0 M.

This volume contains a somewhat general but very readable account of the properties of surface films and the action of the forces responsible for surface tension in effecting a molecular orientation as well as affecting chemical equilibria at interphases. In addition the more important properties of hydrophobic and hydrophilic colloidal systems are discussed.

The particular value of the book lies in the fact that the author has been at some pains to collect and sift the information available on the lipoids. It has, of course, long been a matter of dispute whether the physical functions of biological lipoids are merely to form a lipoid layer possessing all the properties entailed in the acceptance of the hypothesis of Overton and Meyer in respect to cell permeability and narcosis. In many cases these layers must be reduced to the dimensions of monolayers, and in those cases their specific and peculiar properties would appear to be of little value in accounting for the observed phenomena. No detailed examination of the effect of lipoids on proteins in the gel state appears to have been made, but the author has collected together the results of the experiments of Calabek, Meyer, and especially Bamberger on lecithin and cholesterol which appear highly significant. Of recent years the problem of swelling and contraction of amphoteric hydrophilic colloids, such as the proteins in the gel state, has attracted more attention and there is little doubt that the conditions of equilibrium envisaged by Procter and Loeb, namely those determined by the establishment of a Gibbs-Donnan equilibrium, is but part of the story. The restraint placed upon the system expanding on account of the differential osmotic pressure on this theory lies in the inherent extensibility of the network. The work of Astbury and Jordan Lloyd and others has shown that extensibility in solution is determined by the number and nature of the cross linkages, as well as by the balance between the hydrophobic and hydrophilic portions of the polypeptide chains. Increasing the number of cross linkages or decreasing the hydrophilic portions of the chain renders the extensibility in solution less. This is the variable not considered in the formal mathematical investigation. We know, thanks to the work of Kruyt and of Katz, that numerous substances whether ions or organic molecules are adsorbed by the proteins and affect the balance between the hydrophobic and hydrophilic portions of the molecule; thus tannic acid or amyl alcohol reduce the hydrophilic character, whilst thiourea and iodoacetic acid increase the number of hydrophilic groups. We may regard these substances in the terminology of the biologist as antagonistic to each other. It appears from an examination of the data presented by the author that lecithin behaves in a manner similar to thiourea, i.e., it is a hydrophil donator, whilst cholesterol is a hydrophobe donator. A mixture of the two preserves an adjusted equilibrium. If this really be the case the way is paved for the interpretation of many phenomena such as the production of hemolysis by varied reagents.

Eric K. Rideal.

SURFACE ACTIONS OF SOME SULFUR-BEARING ORGANIC COMPOUNDS ON SOME FINELY-GROUND SULFIDE MINERALS

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The fine grinding required to liberate ore minerals so as to permit the fullest application of mineral separation by flotation produces particles of all sizes, from those having a diameter of about 100 microns to those of truly colloidal dimensions. The surface area of the solid phases is large in relation to their bulk, so that actions taking place at the interface between the solids and the liquid in which they are immersed may involve a substantial amount of the agent in question, even though the action—or reaction—does not proceed on the solid to a depth greater than that corresponding to one or two atomic diameters. The physicochemical effect of these reactions on mineral surfaces is known to be tremendous: indeed many of the actual reactions have been surmised from observed physicochemical phenomena.

The action (on the mineral surfaces) of the organic compounds that promote attachment of minerals to gas bubbles is of particular interest to the student of physical chemistry, as the discovery of the actual *modus operandi* may have applications in many fields of colloid chemistry not directly related to flotation. Establishment of the mode of action of these organic compounds—generally called collectors—on the minerals is, of course, of paramount interest to the flotation engineer.

While it is generally acknowledged that collector molecules, being heteropolar, adhere to the mineral surface with their hydrophobic ends oriented away from the mineral, the mechanism of this attachment has been until quite recently a matter of speculation.

The simplest collectors are possibly the fatty acids and their alkali soaps, which are used principally in the flotation of non-sulfide minerals. More complex organic compounds whose molecules contain sulfur, nitrogen, or phosphorus are used for the flotation of sulfide minerals and of the oxidized minerals of lead and copper.

Finely ground apatite[1] abstracts a considerable quantity of palmitate ion from an aqueous solution of sodium palmitate, while quartz does not

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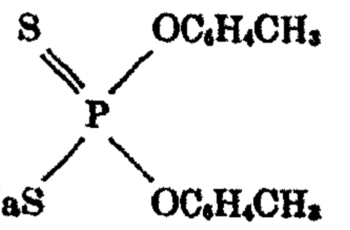
[1] Calcium phosphate in which some phosphate is replaced by fluorine or chlorine; the formula is often stated to be $Ca_5(F, Cl)(PO_4)_3$.

act in this manner. Although quartz sometimes appears to be floatable with sodium oleate as the collector, it has been shown (1a) that flotation takes place to a substantial extent only when quartz has been activated by a cation, such as Pb^{++}, Zn^{++}, Ba^{++}, Ca^{++}, or Fe^{+++}, which is capable of forming an insoluble soap. The fact that oleate ion, as such, adheres only to surfaces that have cations capable of forming insoluble oleates suggests that the mechanism of the abstraction is chemical. The action is practically irreversible and does not take place in accordance with the Freundlich adsorption isotherm (2).

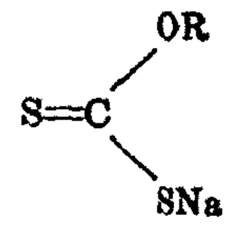
The behavior of some sulfur-bearing collectors, such as xanthates, toward oxidized lead and copper minerals is also well known (1b). These substances react metathetically with the surface of the mineral, forming thereon heteropolar coatings with the water-repellent end of the molecules of the coating oriented toward the water (3).

The mechanism of the action of the sulfur-bearing collectors (e.g., thioureas, mercaptans, thiophenols, or xanthates) on sulfide minerals is less accessible to investigation, and apparently more complicated, than the action of fatty acids and soaps.

In spite of the evidence adduced by Taggart and his associates (4) of the strictly chemical character of the reaction between some collectors and some sulfide minerals, there are investigators who still adhere to the view that the phenomenon is one not involving primary valence forces. Holman (5), for instance, favors the secondary valence theory of adsorption, in that he assumes that xanthate molecules or ions are oriented at the mineral surfaces so that the double-bonded sulfur atoms, which he considers to be air-avid, are away from the mineral surface. Ostwald (6), on the other hand, considers that it is the double-bonded sulfur atom which has an affinity for the mineral, and at least in the case of sodium dicresyl dithiophosphate ("aerofloat"),



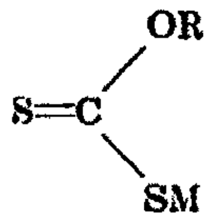
and with xanthates,



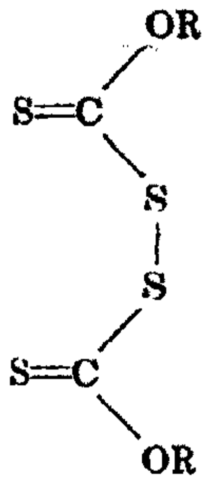
that it is the hydrocarbon group that is hydrophobic. The majority of investigators are in accord with this latter opinion. But Ostwald goes further and imagines that a collector must be "triphilic," that is, that each of its molecules must have a water-avid group, an air-avid group, and a mineral-avid group. Ostwald appears to support the view that the adherence of the reagent is a matter of residual valence.

With those who believe that the abstraction of reagent from solution or suspension by the mineral is the result of a chemical reaction, it is still a question whether the major reaction is with the mineral itself, or with a mineral surface that has become oxidized (Taggart and coworkers), and whether it is the reagent itself, or a product resulting from the oxidation or decomposition of the reagent, which reacts with the mineral.

An investigation of the action of xanthates,



and of dixanthogens,



on galena and pyrite has been conducted at the Montana School of Mines. Work is now in progress in which experimentation is conducted with a wider variety of minerals and reagents.

THE SURFACE REACTIONS OF XANTHATES AND DIXANTHOGENS ON GALENA

In regard to the action of xanthate on galena it is known (3) that: (a) the surface of galena oxidizes rapidly in the presence of moist air or of water exposed to air, to form a film of lead sulfate, basic lead sulfate, or a compound of lead, sulfur, and oxygen of indeterminate composition containing less oxygen in relation to sulfur than the sulfate or basic sulfate; (b) this oxidized coating penetrates cleavage planes to an unknown but substantial extent; (c) the oxidized coating reacts with alkali xanthates, forming lead xanthates, which are less soluble in water than lead sulfate or basic lead sulfate; (d) slightly oxidized galena abstracts xanthate ion from solution and yields sulfate and other anions in approximately equivalent amount.

It was proposed to investigate further the action of xanthates on galena with particular reference to the effect of oxidation on the reaction products. In most cases the galena was finely ground, so that the final surface area of the mineral particles was several hundred times the original area. This made possible the recovery of sizable amounts of reaction products from quantities of galena that were not excessively large. The reaction products were recovered from the mineral by leaching with carefully purified acetone or benzene. The solvent was then evaporated quickly with a fan, so as to prevent as far as possible decomposition of the solute while in solution. Lead xanthates, particularly the higher xanthates and the branching or secondary compounds, are prone to decompose in solution, especially if warm; consequently any method of concentrating the leach liquor by the application of heat, such as distillation, is out of the question.

The raw galena was a jig concentrate from the Tri-State district. Before cleaning (see below) the galena was crushed, concentrated by tabling, and sized to 20/65 mesh by screening. After this preliminary purification the impurities were iron oxides and sphalerite, together with minor amounts of pyrite, calcite and silicates. Of these the ferric oxides were suspected of being the most harmful. However, their removal in the subsequent cleaning step was almost complete.

After the preliminary cleaning just described, the galena was cleaned with an ammonium chloride–hydrochloric acid solution and with 0.5 *N* redistilled hydrochloric acid. The pH of the ammonium chloride–hydrochloric acid stock solution was 1.4, but before use the solution was diluted with thrice its volume of distilled water; a much greater concentration of cleaning solution results in undue metathesis of the hydrochloric acid with the galena, and in precipitation of salts on the mineral.

The galena was washed with distilled water until the rinse was clear, then boiled gently for four hours in 400 cc. of the diluted ammonium chloride–hydrochloric acid solution. The operation was repeated until examination with a binocular microscope showed the galena to be substantially free from impurities other than a little quartz, pyrite, and sphalerite; total impurities usually were about 0.3 per cent. The sample was next boiled gently for two hours with 400 cc. of 0.5 *N* hydrochloric acid, and then was washed with distilled water. The hydrochloric acid treatment and subsequent washing were repeated.

The object of this procedure was to remove the lead sulfate coating from the galena surface and to dissolve ferric impurities. This method was preferred to the use of ammonium acetate, for it was thought ammonium acetate might contain organic impurities difficult to remove. Also, hot hydrochloric acid (7) dissolves lead sulfate, especially if a large concentration of chloride ion is maintained by the addition of an alkali chloride or ammonium chloride.

After the special cleaning treatment just described, the mineral was ground in a closed porcelain jar of the type known as an assay mill. The jar was filled half-way with pebbles and pulp, the remainder of the space being occupied by air. In some tests a nitrogen atmosphere was used; this is specifically stated in every instance. Every grind was, of course, a wet grind.

It was found that galena treated in this manner abstracts almost as much xanthate after it is ground as galena that has not been cleaned. This indicates that galena almost completely reoxidizes on a few hours' exposure to air. The amount of oxygen in an assay mill is of an order of magnitude sufficient to oxidize the fresh galena surface produced by a six-hour grind.

The following experiments were singled out from among many as of especial significance in ascertaining the true action of xanthates and dixanthogens on galena.

Experiment No. 1

Five hundred grams of cleaned galena was ground for six hours in the presence of 500 cc. of water; 2.50 g. potassium ethyl xanthate was added to the pulp of ground mineral. The mixture was stirred, allowed to stand for fifteen minutes and filtered. It was found by titration that approximately 1.0 g. of the reagent remained in the filtrate in the form of potassium ethyl xanthate; in other words, ethyl xanthate ion corresponding to 1.5 g. of molecular potassium ethyl xanthate had been abstracted or decomposed.

After dewatering, the treated mineral was leached with nearly one liter of acetone; about one-half of the acetone was stirred with the mineral for fifteen minutes, and the mixture was filtered, and the rest of the acetone was used in washing the filter cake. The filtrate was evaporated with an electric fan. During the process characteristic crystals of lead xanthate (8), arranged in lily-pad fashion, appeared on the surface of the leach liquor. Besides the lead xanthate, there was found in the leach residue some oil, possibly ethyl dixanthogen, and a trace of lead sulfide, but no potassium ion. Methods of identification of these and other leach residues are presented elsewhere (8).

This experiment was repeated, except that 1.50 g. of xanthate was used in place of 2.50 g. Only 0.22 g. of potassium xanthate was found in the aqueous filtrate, hence 1.28 g. was abstracted by the mineral. The dewatered, treated mineral contained the same substances as before.

This experiment was again repeated, except that the amount of xanthate was reduced further to 1.0 g., and that the grinding time was increased to eight hours. All the xanthate was abstracted. The dewatered, treated mineral contained the same substances as before.

These experiments show that xanthate ion corresponding to one gram or more of potassium ethyl xanthate is abstracted in fifteen minutes by

500 g. of galena ground from six to eight hours in contact with a limited volume of air. These experiments also show that a considerable excess of xanthate ion is required to increase greatly the amount abstracted.

Experiment No. 2

Experiment No. 1 was repeated, except that the grinding time was increased threefold to eighteen hours. Of 2.50 g. of potassium ethyl xanthate added initially, but 0.42 g. remained in the aqueous filtrate, indicating that xanthate ion corresponding to 2.08 g. of the agent had been abstracted or decomposed. In this case the amount of xanthate abstracted did not increase in proportion to the added surface produced by the longer grind (9). This is perhaps because some of the freshly produced surface was not completely oxidized, and therefore did not react to the extent that a completely oxidized surface would react.

Experiment No. 3

Five hundred grams of cleaned galena was ground for eighteen hours in the presence of 1.00 g. of potassium ethyl xanthate. The xanthate ion disappeared completely. However, the amount of lead xanthate recovered from the treated mineral was very small. In this case the xanthate had apparently decomposed, either while in the solution or while at the mineral surface as solid xanthate. In this, as in other tests in which the mineral was ground in the presence of the reagent, various decomposition products were noted, especially an oil, possibly ethyl dixanthogen, and elemental sulfur, and perhaps lead ethyl mercaptide (8).

This test shows that potassium ethyl xanthate or lead ethyl xanthate decomposes much faster if in association with a galena surface, moisture, and atmospheric gases than if in bulk in the solid state or in pure aqueous solution or suspension.

Experiment No. 4

Five hundred grams of cleaned galena was ground four hours and then treated with 2.00 g. of potassium *n*-amyl xanthate, in place of ethyl xanthate. Lead *n*-amyl xanthate was the chief product extracted by leaching the mineral.

This test shows that the primary reaction between dissolved xanthate and galena is the same whether *n*-amyl or ethyl xanthate is used.

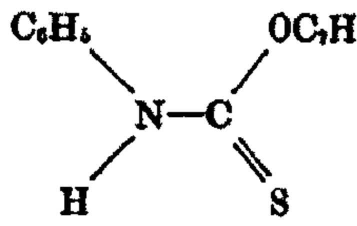
Experiment No. 4a

Experiment No. 4 was repeated except that the amount of xanthate was reduced to 1.00 g., and that, after treatment, the mineral was exposed in aqueous pulp to the atmosphere for a day before filtering. As the galena was unusually dry after this treatment, it was leached with benzene instead of acetone. Sulfur corresponding approximately to one sulfur atom per xanthate molecule abstracted was the only product identified; however, a strong odor suggestive of a mercaptan or of a xanthic ester was noted.

These tests show that lead amyl xanthate decomposes rapidly, and in a well-defined way, when in contact with lead sulfide, moisture, and air.

Experiment No. 4b

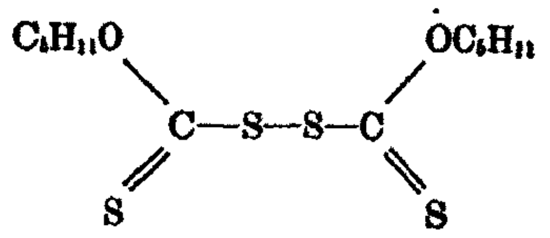
Experiment No. 4a was repeated with phenyl thiourethan,



used in place of xanthate. Sulfur corresponding to approximately one atom per molecule of reagent was obtained in the leach liquor.

Experiment No. 5

One hundred grams of uncleaned galena, ground thirty hours with 400 g. of granite in the presence of *n*-amyl dixanthogen,

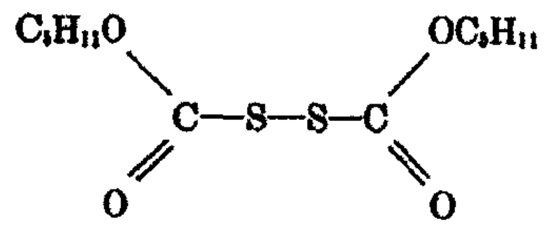


was floated, filtered, and then leached with benzene. The benzene left a residue of sulfur plus some volatile material, possibly the amyl ester of amyl xanthic acid (8). The amount of sulfur recovered was approximately that which would be contributed by two of the sulfur atoms in each dixanthogen molecule.

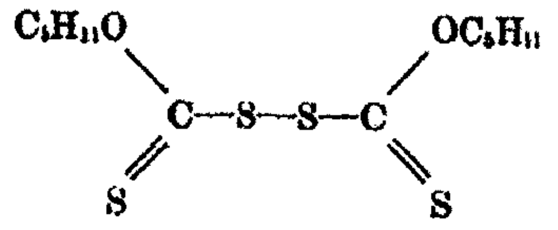
This test shows that dixanthogen, which is the direct oxidation product of xanthate, is itself decomposed when allowed to remain in contact with a large amount of galena surface.

Experiment No. 5a

If amyl formate disulfide,



be substituted for amyl thioformate disulfide (amyl dixanthogen),



sulfur appears again as the only solid reaction product. The amount of sulfur obtained is again approximately that corresponding to two sulfur atoms per molecule of reagent, showing that in this case, as probably in that involving dixanthogen, the sulfur left with the mineral after reaction is the single-bonded, or disulfide, sulfur.

Experiment No. 6

Seven hundred grams of uncleaned galena was ground for four hours in an atmosphere of nitrogen in the presence of 1.00 g. of potassium ethyl xanthate which had been added in oxygen-free solution. The assay mill was emptied in a nitrogen atmosphere, and the slime was filtered and washed with acetone, also in an atmosphere of nitrogen.

The aqueous filtrate was titrated immediately for xanthate. It was found that xanthate ion corresponding to 0.99 g. of the reagent had disappeared. Sulfate ion was found in the aqueous filtrate, and lead xanthate was recovered from the treated mineral.

A similar experiment was conducted with cleaned galena in a nitrogen atmosphere. Again a substantial disappearance of xanthate ion was noted. Xanthate disappearance, sulfate evolution, and lead xanthate extraction from the mineral were much smaller in this experiment than in corresponding experiments conducted in air.

Taken as a whole these experiments confirm the view of Taggart and his associates, in so far as galena and xanthates are concerned, that the reaction is essentially a metathesis between oxidized coatings on the mineral and the xanthate in solution, although they do not exclude the possibility of reaction between galena itself and the xanthate in solution.

From the experiments described in this paper, it would appear that the following reactions take place:

1. Galena + oxygen → lead sulfate coating on galena.
2. Galena coated with lead sulfate + potassium xanthate in aqueous solution → galena coated with lead xanthate + potassium sulfate in solution.
3. Lead xanthate coating on galena + oxygen (?) → dixanthogen coating on galena + oxidized lead salt.
4. Galena not coated with lead sulfate + dixanthogen suspended in pulp → galena coated with dixanthogen.
5. Dixanthogen coating on galena + oxygen (?) → elemental sulfur corresponding to the two single-bonded (disulfide) atoms of sulfur per dixanthogen molecule + volatile sulfur organic compounds (xanthic esters and mercaptans?).

The reactions are purposely not formulated because of the uncertainty which at present surrounds some of them. It appears that steps 2 and 5 are relatively rapid, that 3 is rather slow, and that the speed of 4 depends on physical rather than chemical circumstances.

THE SURFACE REACTIONS OF XANTHATES AND DIXANTHOGENS ON PYRITE

From what is known concerning galena it is tempting to conclude that similar reactions take place with other sulfide minerals. In the case of pyrite, however, it is difficult to postulate the formation of iron xanthate as a first step in a chain of reactions because ferrous xanthate is quite soluble[2] and because ferric xanthate hydrolyzes to ferric hydrate and xanthic acid.

Since, however, xanthates are very effective in floating pyrite, and since xanthates are abstracted by the mineral, it is evident that xanthate ion or some decomposition product must attach itself to the surface of the mineral. The most probable substance seems to be dixanthogen. The experiments described in the following pages, however, indicate that the reactions involved are somewhat more complicated than is implied by the view that the active collector is dixanthogen.

The experimental procedure for testing pyrite was essentially the same as that used in Experiment No. 1, in which galena was used. The pyrite was hand-picked mineral from Butte. After being cleaned it contained a trace of arsenic, less than 0.05 per cent copper, and no zinc.

The pyrite was cleaned with 1:1 hydrochloric acid according to the method recommended by C. W. Orr (12) except that the mineral was first washed, at a coarse size, with redistilled acetone. This step was designed to remove oily compounds possibly deposited from suspension in air while the mineral was stored in the laboratory (3). Unless otherwise stated, the experiments were performed in air and a 500-g. sample of pyrite was used in each case. All the grinds were wet grinds; during grinding the pulp dilution was 1:1.

Experiment No. 7

To 20/65 mesh cleaned pyrite ground for eight hours was added 1.00 g. of potassium ethyl xanthate. Immediately after the addition of xanthate there was an odor resembling that of commercial carbon disulfide. The xanthate was completely abstracted or destroyed. The aqueous filtrate contained ferric ion, chloride ion, sulfate ion, but no sulfide ion.

The acetone leach liquor contained elemental sulfur.

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[2] The solubility of ferrous ethyl xanthate exceeds one part per thousand, whereas the solubility of lead ethyl xanthate is less than one part per million.

Experiment No. 7a

Experiment No. 7 was repeated, except that the pulp was allowed to stand in the assay mill for two days before opening the mill. A much stronger vacuum than usual was noted on opening the mill. This indicates that the freshly produced pyrite surfaces, the reagent, or both had been more completely oxidized by the oxygen in the mill than if the mill had been opened immediately.

Besides sulfur, the following substances appear to have formed during the reaction:—carbon dioxide, carbon disulfide, carbonyl sulfide, and a relatively complex organic acid (8).

These experiments show that potassium ethyl xanthate is abstracted by pyrite ground in a limited volume of air, from a pulp slightly acid in the vicinity of the mineral particles, probably because of oxidation of the pyrite, to yield principally elemental sulfur, but also miscellaneous volatile organic compounds as yet incompletely determined.

Experiment No. 8

Acid-cleaned pyrite was ground eighteen hours with 2.00 g. of potassium *n*-amyl xanthate. The aqueous mixture was agitated with redistilled benzene in a closed jar, on agitating rolls. All the pyrite went into the benzene phase. The benzene was evaporated with a current of air; the resulting residue contained sulfur and something that smelled like an ester.

This experiment shows that the reactions with amyl xanthate are similar to those with ethyl xanthate.

Experiment No. 9

Five hundred grams of cleaned pyrite and 1 g. of ethyl dixanthogen in 20 cc. of ethyl alcohol was added to one-half liter of water. The mixture was ground for six hours. The mill was opened and a sample of the pyrite, which formed a dry froth (14), was immediately shaken with ether and the sample was tested for dixanthogen. No dixanthogen or xanthate was found,—only sulfur. The amount of sulfur recovered from the total pulp was 0.210 g., which corresponds nearly to two atoms of sulfur per dixanthogen molecule.

This experiment shows that dixanthogen in contact with pyrite is decomposed to yield elemental sulfur.

Experiment No. 10

Five hundred grams of pyrite was ground twelve hours in a normal potassium hydroxide solution. After this preliminary grind 1 g. of ethyl dixanthogen was added and the mixture was ground further for eight hours. The leach liquor contained some oil, possibly dixanthogen, together with sulfur. The sulfur was less abundant than in experiments conducted in pulps not made alkaline.

This experiment suggests that if the sulfuric acid formed by the reaction of atmospheric oxygen with pyrite in the presence of water is neutralized and an excess of alkali is present, the dixanthogen may not decompose so readily, nor perhaps be abstracted so readily.

Experiment No. 11

Five hundred grams of cleaned pyrite was ground for six hours to be tested as a blank. In the acetone leach there was found a small amount (less than 0.020 g.) of sulfur and traces of ferric chloride. The amount of sulfur found was less than one-tenth the amount found in corresponding experiments with a xanthate or dixanthogen.

This experiment shows that the sulfur observed in experiments 7 to 10 is essentially not an impurity derived from the mineral.

Experiment No. 12

Seven hundred grams of uncleaned pyrite was ground in a nitrogen atmosphere to parallel experiment No. 6 carried out with galena, except that amyl xanthate was used in place of ethyl xanthate. Of the 0.991 g. of xanthate added, 0.986 g. was abstracted or decomposed. Less sulfur was found than in other experiments, and the sulfur was sticky with an oil.

This experiment shows that amyl dixanthogen is formed when amyl xanthate is added to pyrite, but that the dixanthogen is subsequently decomposed to yield sulfur.

From the above experiments it is clear that the product of the reaction of a xanthate with pyrite, or of a dixanthogen with pyrite, is in the end sulfur, together with some as yet incompletely identified volatile compounds. If the quantity of oxygen or other oxidizing agent is minimized, the reaction chain may be limited merely to the production of dixanthogen.

It is not known whether xanthate ion is adsorbed momentarily at the pyrite surface where it becomes oxidized to dixanthogen, or whether soluble iron salts are responsible for the change of the xanthate in solution. In the absence of definite evidence as to the mode of oxidation of the xanthate, the following reaction steps appear likely:

1. Pyrite + oxygen + xanthate ion → dixanthogen-coated pyrite + sulfate ion;
2. Pyrite + dixanthogen suspension in water → dixanthogen-coated pyrite;
3. Dixanthogen-coated pyrite + oxygen → sulfur + miscellaneous volatile compounds.

THE SURFACE REACTIONS OF OTHER SULFIDE MINERALS

Preliminary experiments in need of duplication and extension have been conducted with chalcocite, Cu_2S, chalcopyrite, $CuFeS_2$, and sphalerite, ZnS. In view of the interest presented by these incomplete experiments, some of the results are presented here.

Sphalerite does not abstract xanthates from solution (1d); no reaction product can be extracted from the mineral.

Chalcocite abstracts isoamyl monosulfide from aqueous suspension. Part of the reagent, unchanged, can be extracted from the treated mineral.

Chalcocite abstracts isoamyl disulfide from aqueous suspension. The reagent is changed to the monosulfide and sulfur.

Chalcocite abstracts isoamyl mercaptan from aqueous suspension or solution. The reagent appears changed to isoamyl monosulfide and sulfur (13).

Chalcopyrite abstracts isoamyl monosulfide from aqueous suspension. The reagent appears changed to a mixture of sulfur and an oily substance as yet unidentified.

SUMMARY

Much work remains to be done to complete the investigation which has been undertaken. However, the following conclusions summarize the results obtained so far.

1. Galena reacts with xanthates to form lead xanthates, principally by metathesis of oxidized coatings with the xanthate. Subsequently the xanthate changes to sulfur and unidentified oils. Some of the changes appear to require atmospheric oxygen. Because of the great area over which the lead xanthate or dixanthogen is assumed to be spread, the galena may well be regarded as a catalyst in the decomposition of the primary reaction product.
2. Galena abstracts dixanthogen from aqueous suspension, and apparently catalyzes the decomposition or oxidation of the dixanthogen to yield principally elemental sulfur.
3. Pyrite, or ferric ion derived from it by oxidation, changes xanthate to dixanthogen; the dixanthogen can be extracted from the mineral surface provided oxidation of the dixanthogen is prevented.
4. If oxidation at the surface of pyrite is not restricted, the dixanthogen formed there by preliminary oxidation of xanthate, or that abstracted directly from a suspension of dixanthogen, breaks down to elemental sulfur and miscellaneous volatile compounds.
5. Reactions of the copper and zinc sulfides appear to be different from those of galena and pyrite. In general, indeed, it may be said that each mineral-reagent combination requires a special investigation.

The writers wish to express their appreciation to Mr. M. S. Hansen and Mr. L. J. Hartzell, Jr., for the use of unpublished data.

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FREEZING POINTS AND OSMOTIC PRESSURES OF LACTOSE SOLUTIONS

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In what ratio of equivalence lactose may be substituted for sucrose in solutions in which the essential effect of the sugar present is dependent on osmotic pressure, is the question this work was undertaken to answer. Since osmotic pressure is proportional to the number of discrete units of solute in a solution, it is to be expected that anhydrous lactose would be exactly equivalent to sucrose on a weight basis, provided only that the two sugars are associated, dissociated, or hydrated in water solution to the same degree. Preliminary calculations of osmotic pressures of sucrose solutions showed that values derived by the gas law formula differ from those derived from freezing point measurements of Pickering (4) in such a way as to be explicable by the assumption of hydration of each sugar molecule by three to six molecules of water, the exact number depending on the concentration of the solution. It seemed reasonable to expect that a similar, though not necessarily identical, situation would be found to exist for lactose solutions. In any case, actual measurements were desirable.

Freezing points of lactose solutions were determined by the Beckmann method with the usual precautions. Several samples of purified lactose were used, each sample having been dried separately. The checking of results by use of different samples was taken to indicate a satisfactory degree of purity of all the samples. The lactose for each determination was weighed into a Florence flask, the required quantity of water added by means of a pipet, and the flask warmed until solution was complete, care being taken to minimize loss of water by evaporation. The solution was then transferred to the freezing tube and a freezing point determination made.

Particularly at the higher concentrations it frequently happened that crystallization of sugar would begin before freezing of water had commenced. This could be detected by the continuing rise of the mercury thread in the thermometer during separation of solid material, and could be verified by removing the freezing tube and observing whether the crystals in the solution were lactose or ice. Repeated efforts to obtain freezing points on solutions of concentrations higher than the highest recorded in the table were unsuccessful because the crystallization was initially of lactose. The values recorded in table 1 are the averages of the results of at least three determinations in each case.

TABLE 1

Freezing points and osmotic pressures of lactose solutions

WEIGHT OF ANHYDROUS LACTOSE IN 100 GRAMS WATER	FREEZING POINT Δ	OSMOTIC PRESSURE 11.898 × Δ
grams	*degrees C.*	*atmospheres*
4.738	−0.280	3.33
9.452	−0.557	6.63
14.144	−0.839	9.98
18.812	−1.125	13.39
23.451	−1.426	16.96
28.567	−1.731	20.59
37.897	−2.353	28.02
47.201	−2.986	35.52
56.436	−3.672	43.68
65.594	−4.344	51.68

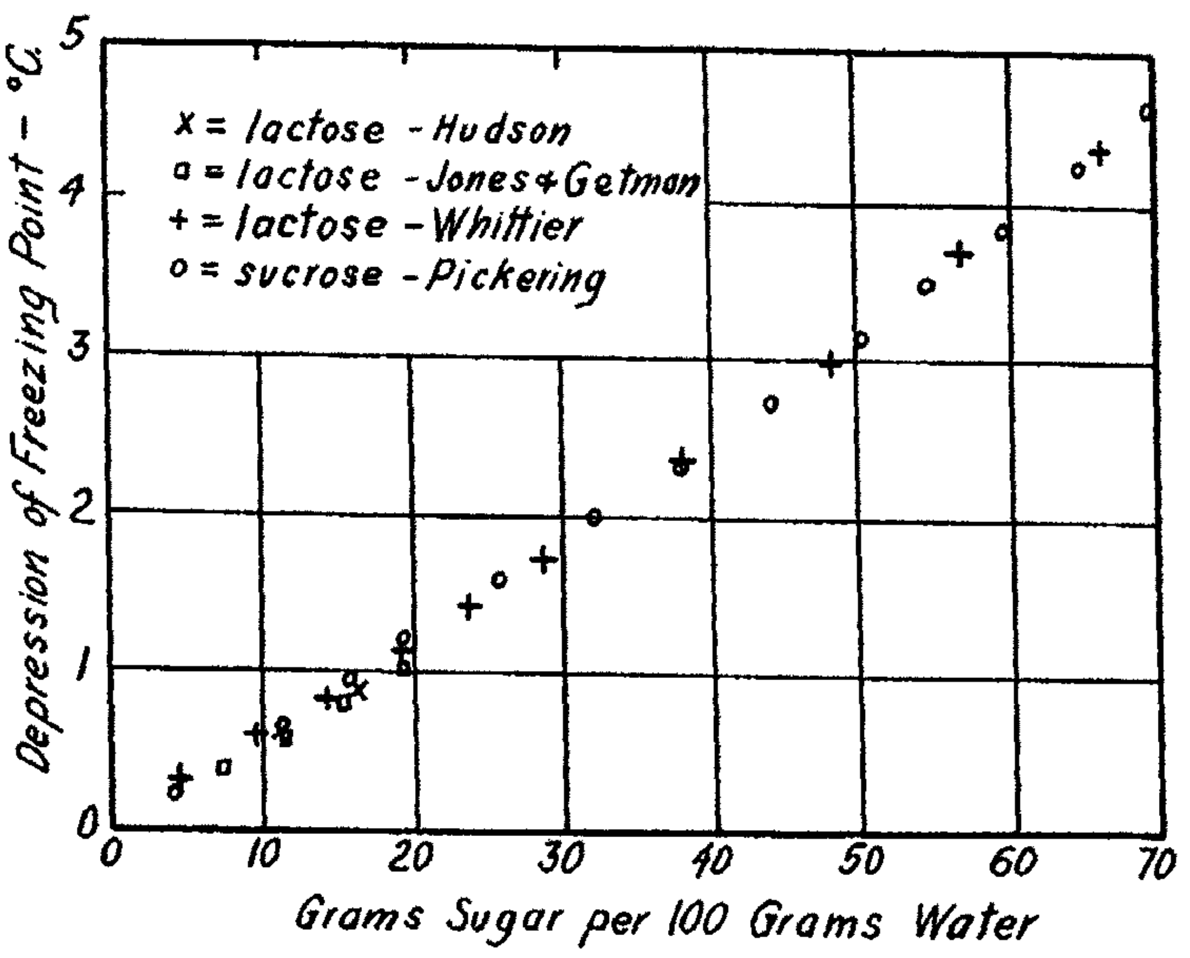

FIG. 1. FREEZING POINT DEPRESSIONS OF SOLUTIONS OF LACTOSE AND OF SUCROSE

The concentrations used were prepared by dissolving 5 g. or some multiple of 5 g. of lactose hydrate in 100 g. of water. These concentration values were corrected for the effect of undercooling by means of the formula

$$w_a = \frac{w}{1 - \frac{ct}{L}}$$

in which w is the weight of lactose hydrate originally present in 100 g. of water, w_a is the weight of lactose hydrate present in 100 g. of water at the moment the thermometer thread has risen to the freezing point after undercooling, t is the amount of undercooling in degrees Centigrade, c is the specific heat of the liquid in calories, and L is the latent heat of fusion of ice in calories. The concentration of anhydrous lactose was next calculated by means of the formula

$$w_b = \frac{342}{360} \cdot w_a \cdot \frac{100}{100 + \frac{18}{360} \cdot w_a}$$

in which w_a has the same significance as above, and w_b is the weight of anhydrous lactose in 100 g. of water.

The factor used for calculating osmotic pressure from depression of freezing point, 11.898, is that given by Levalt-Ezerskii (3) for sucrose. The justification for applying this value to calculations involving lactose is the chemical similarity of the two compounds and the close agreement of freezing points of their solutions. This agreement is shown in figure 1, in which Pickering's (4) values of freezing points of sucrose solutions are plotted together with values for lactose by Hudson (1), by Jones and Getman (2), and by the author.

The values of osmotic pressure given in table 1 are in all cases greater than values calculated from the gas law relationship, $\frac{22.4}{342} \times 10\ w_b$, the difference being proportionately greater at the greater concentrations. Since values for lactose agree with values for sucrose within 1 per cent and since, as established by freezing point determinations on a solution containing both sugars, the osmotic pressures of the two sugars are additive, it is concluded that one may be substituted for the other in solutions without appreciable influence on osmotic effects.

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II. THE ADSORPTION OF THORIUM B BY THALLIUM HALIDE CRYSTALS IN THE PRESENCE OF VARIOUS IONS

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INTRODUCTION

In formulating the precipitation and adsorption rules (1) of Paneth, Fajans, and Hahn, much work has been done on the adsorption of various ions of common elements, of radioactive elements, and of dyes on silver and mercury salt crystals. Relations have been shown between adsorbability and insolubility, adsorbability and mixed crystal formation, and adsorbability and weakness of dissociation of the compound formed by the adsorbed ion. It has been our purpose to extend this study to thallium halide crystals. In this paper measurements made on the adsorption of thorium B by thallium bromide and thallium iodide crystals and the effect of various anions and cations on this adsorption will be reported.

The polar crystals of thallium bromide and thallium iodide are of the cubic system of the cesium chloride type, where a thallium ion is surrounded by eight halide ions. The surface ions in the lattice possess a residual attractive force which is available for attaching to the crystal ions which fit into the crystal lattice, or which form an insoluble or undissociated compound with the oppositely charged ions of the lattice. When thallium iodide is in equilibrium with its saturated solution, adsorption of its own ions is analogous to crystal growth. When thallium iodide crystals are in contact with a solution of an iodide salt, they take on a minus charge owing to the adsorbed iodide ions and when they are in contact with a solution of a thallium salt, they take on a plus charge owing to the adsorption of the thallium ions. If a thallium iodide crystal is in contact with its saturated solution and has a preferential adsorption for one of its own ions, the surface of the crystal will take on the charge of the ion which has been adsorbed. In the case of silver iodide, Lange and Crane (2) found that silver iodide had adsorbed iodide ion from the saturated solution and that the silver iodide–saturated solution potential was 0.004 volt. It was necessary to bring the silver iodide crystal to equilibrium with a 4×10^{-6} normal silver nitrate solution in order to neutralize this minus charge on the crystal. Bromide ion is less readily adsorbed to silver bromide crystal surfaces and chloride ion less so than bromide ion. In this series of halide ions, the adsorbability of the ions on the silver halide crystal is (1) in the inverse order of the solubility of the salts formed by the ions, (2) in the same order of the deformability of the ions, and (3) in the inverse order of the hydration of the ions. Fajans considers these three factors of prime importance in determining the relative adsorbability of similar ions.

We have found in the case of the purest thallium iodide which we could prepare that the iodide ion was preferentially adsorbed, giving the thallium iodide crystal a negative charge. This "neutral" thallium iodide crystal showed a marked adsorption for thorium B ions and in colloidal suspension migrated toward the positive terminal when viewed in the field of a microscope. In comparing the relative adsorbability of the halide ions, we found that iodide ion was more easily adsorbed than bromide ion and bromide ion more easily adsorbed than chloride ion on thallium halide crystal surfaces.

Fajans has found in the case of the relative adsorbability of dissimilar ions that other factors than those just mentioned are also of importance (3). Even though silver erythrosinate is one hundred times more soluble than silver iodide, the erythrosinate ion is much more easily adsorbed than is iodide ion on silver iodide. In this case he states that there is a dominating influence of the non-polar forces in the large dye ion. He also finds that thiocyanate ion is better adsorbed on silver iodide than is bromide ion even though silver bromide is less soluble than is silver thiocyanate.

PREPARATION OF MATERIALS

Water

Water for all the experiments was made by use of a Barnstead still. By keeping the condenser water hot, water with a conductance of 1.7×10^{-6} to 2×10^{-6} was easily obtainable. This water was stored and used in Pyrex containers which had been thoroughly steamed out. In the washing of the crystals, the water was piped directly from the block tin condenser of the still to the washing tower shown in figure 1. Thus it was possible to wash the precipitated crystals over long periods of time with pure water with no possibility of contamination by foreign ions. In the case of the silver salts used in the work to be described in the next paper, the water was run through the wall of a dark room so that the silver halide crystals could be washed continuously with agitation in the dark with water of the conductance given above.

Thallium bromide and thallium iodide

In the earlier work on the adsorption of ions on precipitates, the adsorption was allowed to take place as the precipitate was formed. For instance, to a silver nitrate solution containing thorium B ions or dye ions was added potassium bromide solution until the equivalent point was reached, or to such a point that there was a definite excess of silver ions or bromide ions. The solution was then freed from the precipitate by filtering or centrifuging and the concentration of the thorium B or dye ions was determined in the solution. Obvious possible errors could be caused by (1) the presence of the potassium or the nitrate ions; (2) the difficulty of forming the precipitate each time in such a way as to have the same surface; (3) the difficulty of preventing local excesses of either ion, which would result in local charges on the precipitate; and (4) the possibility of the occlusion of thorium B (either as ions or in some colloidal or pseudocolloidal form) or the dye ions in the precipitate.

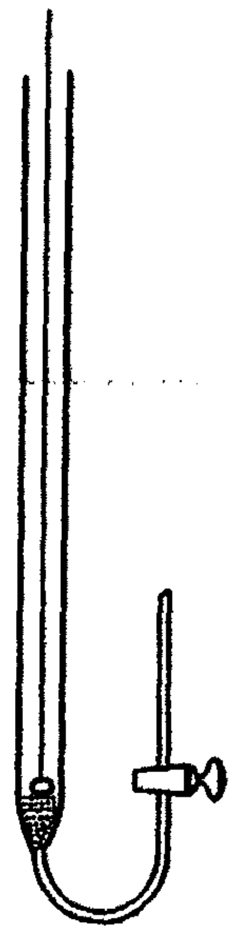

FIG. 1. WASHING TOWER

The results of such work could be treated more qualitatively than quantitatively. Beekley and Taylor used a suspension of thoroughly washed silver iodide as adsorbent. Here there is the possibility of a changing surface of the precipitate owing to small crystals going into solution and recrystallizing on large crystals. They report a change of 50 per cent adsorption in six months time. J. Walker made use of silver bromide powder, and in the latest work of Fajans (4) the crystals used were prepared as a perfectly dry powder and a definite weight was always used in the adsorption experiments. This method has the advantage of obtaining reproducible surfaces which undergo slight changes in the few minutes needed to reach the adsorption equilibrium. A large amount of powder can be prepared and preserved over a long period of time, thereby assuring the same surface per unit of weight for a number of experiments.

The thallium bromide and thallium iodide crystals were prepared by three methods in order to study the behavior of the so-called "neutral particle." Hahn (5) reports that it is possible to prepare crystals whose surfaces are electrically neutral and that such crystals have no adsorption for radioactive ions. Our crystals prepared by the three methods to be described all possessed a marked adsorption for thorium B ions.

First method. Two liters each of 0.1 *N* thallium nitrate and potassium bromide or potassium iodide were allowed to drop at equal rates into 4 liters of water contained in a large balloon flask. The water was rapidly stirred. The precipitated salt was then allowed to settle and the supernatant liquid was siphoned off. The precipitate was washed by decantation ten times with 4-liter portions of water. It was then warmed and rapidly stirred with 4 liters of water for 15 minutes. This treatment, according to Hahn, will dissolve from the surface any adsorbed ions. The solution was cooled, and the supernatant liquid decanted. This warming procedure was repeated three times. Then the precipitate was placed in the washing tower shown in figure 1 and agitated as some 60 liters of water were slowly passed through the crystals from below. No test for nitrates was obtained when 20 cc. of the wash water was evaporated to dryness and the phenolsulfonic acid test was used. The washed crystals were then dried on a thoroughly cleaned porous tile and warmed to 60°C. to 110°C. in an electric oven. The crystal powder was stored in a crystallizing dish over phosphorus pentoxide in a desiccator.

Second method. The potassium bromide or iodide solution was first added to the water as above and the thallium nitrate solution was dropped in with rapid stirring. The precipitated powder was then put through the same steps as given above.

Third method. The thallium nitrate was first added to the water and the potassium bromide or iodide solution was dropped in with rapid stirring. The rest of the procedure was carried out as stated.

Thorium B nitrate solution

Thorium B was collected as described in the paper of King and Romer (1). After about sixty-four hours the loops were removed and the thorium B was dissolved in 5 cc. of warm 0.2 *N* nitric acid. This solution was then washed into a 100-cc. volumetric flask, 13 cc. of 0.2 *N* nitric acid added, and the whole made up to 100 cc. with water. One cc. of this solution was then removed, evaporated to dryness, and its activity determined in a beta ray electroscope. The volume was then adjusted with nitric acid of equal concentration so that 1 cc. of the resultant solution when evaporated to dryness had an activity of approximately 150 scale divisions per minute. This constituted the stock solution of thorium B nitrate.

Thallium nitrate stock solution

A thallium nitrate solution slightly more concentrated than 0.2 *N* was prepared. This was standardized gravimetrically by precipitating thallium iodide in 50 per cent alcoholic solution. The solution diluted to 0.2 normal was used as the stock solution of thallium nitrate.

Potassium bromide stock solution

A 0.2 normal potassium bromide solution was prepared by standardization with silver nitrate using potassium chromate as an indicator.

Potassium iodide stock solution

A 0.05 normal solution of potassium iodide was prepared by standardizing gravimetrically by precipitation of silver iodide (dark room).

Potassium chloride stock solution

A 0.05 normal solution of potassium chloride was prepared by titration against silver nitrate solution using potassium chromate as an indicator.

Potassium thiocyanate stock solution

A 0.05 normal solution of potassium thiocyanate was prepared by titration against test silver dissolved in nitric acid, using ferric alum as an indicator.

Potassium chromate stock solution

A 0.05 molar potassium chromate solution was prepared by treatment with sulfuric acid and potassium iodide and titration of the liberated iodine with standard sodium thiosulfate solution.

Chromic acid stock solution

A 0.05 molar chromic acid solution was made by dissolving chromium trioxide in water and titrating against sodium hydroxide with phenolphthalein as indicator.

Potassium phosphate stock solution

A 0.05 molar potassium phosphate solution was made according to the gravimetric method given in Griffin, Technical Methods of Analysis, page 764.

Phosphoric acid stock solution

The phosphoric acid solution was 0.05 molar and was standardized against sodium hydroxide using methyl orange and phenolphthalein as primary and secondary indicators.

Potassium oxalate stock solution

The 0.05 molar solution of potassium oxalate was prepared by standardization against potassium permanganate in acid solution.

Silver nitrate stock solution

The 0.2 normal solution of silver nitrate used was prepared by titration against standard potassium thiocyanate solution, using ferric alum as an indicator.

Lead nitrate stock solution

A 0.098 normal lead nitrate solution was standardized according to Olsen, Quantative Analysis, page 75.

Cupric nitrate stock solution

A 0.02 normal copper nitrate solution was prepared by standardization in the electrolytic deposition of the copper.

The watch glasses

The watch glasses used were matched in sets, each watch glass in a set having approximately the same diameter, curvature, and thickness. It is important in the activity measurements that the radioactive material be always in a thin layer of a salt deposited uniformly on these watch glasses and that this layer be always the same distance from the aluminum window of the electroscope. A varying distance from the aluminum window of the electroscope causes errors not only because of the different absorption in the air layer but also because of the scattering effect of the beta particles. A thin, even deposit of active salt is essential for duplication of measurements. This meant that the evaporation of the samples on the watch glasses had to be controlled. More soluble salts precipitated out more readily than less soluble salts. The evaporation was carried out on a water bath heated by controlled electrical heaters. The water bath was level. The watch glasses containing the active solutions were leveled and a regulated volume of air was blown over the surfaces by an electric fan. Special attention was given here to a series of evaporations so that the control experiment as well as the rest of those in the series had the same treatment in the evaporation procedure.

The bottles

The bottles used for shaking were about 40 cc. in volume and fitted the centrifuge cups so that no transfer of solution was necessary.

The pipettes used were either standardized by the Bureau of Standards or standardized by weighing their content of water.

The cleaning of glassware

All glassware in the work was allowed to stand for one hundred hours or more after using so that there was very slight residual activity. The glassware was then allowed to stand in concentrated chromic acid and sulfuric acid to remove traces of impurities and grease. It was then rinsed with distilled water and the special water of low conductivity. Grease on the watch glasses caused the solutions to evaporate unevenly, giving activities which could not be reproduced. The bottles were steamed out between measurements.

The electroscope

The electroscope used was described in the work of King and Romer (1). It was calibrated and adjusted so that different parts of the scale were equal, but for most of the work the same part of the scale was used so as to eliminate errors due to change in calibration. The procedure of King and Romer (1) was employed in all the activity measurements.

METHOD OF PROCEDURE

The carefully dried powder was weighed out into each bottle. Different volumes of water and of the solutions of the ions being studied were added, making the total volume of solution 25 cc. To this was added 5 cc. of a nitric acid solution of thorium B. The amount of nitric acid in the thorium B solution was such that the total volume of 30 cc. was always 0.006 normal in nitric acid. The bottles were then closed with glass stoppers, placed in a shaking machine, and shaken for one hour. The bottles were next placed in the centrifuge and centrifuged for 15 minutes at 1500 r.p.m. Without disturbing the precipitate, a dry 5-cc. pipette was rinsed out with the clear solution. Then two 5-cc. portions of the solution were pipetted out on watch glasses and dried by evaporation in a stream of air. The dried precipitate on the watch glass was then allowed to stand for eight hours or until radioactive equilibrium had been reached. For each series of solutions a measurement was made on a "control." Bottles containing 30 cc. of the solution as made up above without the powder were handled identically and the activity of 5-cc. portions measured. All activities were calculated to T_0 for comparison.

EXPERIMENTAL RESULTS

1. The effect of bromide ion on the adsorption of thorium B by thallium bromide

Five-tenths of a gram of thallium bromide, prepared by the first method, were used as adsorbent. Two series were run. All measurements in series

I were calculated to T_0' and those of series II to T_0''. The results are given in table 1 and the data is plotted in figure 2.

2. *The effect of centrifuging*

A series of experiments was carried out to determine if there was any effect introduced into the work by the centrifuging step in the procedure.

TABLE 1

The effect of bromide ion on the adsorption of thorium B by thallium bromide

THALLIUM BROMIDE	POTASSIUM BROMIDE	ACTIVITY CORRECTED TO T_0	ADSORPTION
Series I. 3 millimoles of nitric acid per liter			
gram	*millimoles per liter*	*scale divisions per minute*	*per cent*
0	0	44.8	
0.5	0	26.6	40.7
0.5	1.66	25.5	43.1
0.5	3.33	24.7	44.9
0.5	5.0	24.4	45.6
0.5	6.6	23.9	46.7
0.5	8.33	23.6	48
0.5	10.0	22.6	49.6
Series II. Same concentration of nitric acid			
0	0	40.3	
0.5	0	23.9	40.7
0.5	1.66	23.1	42.7
0.5	3.33	22.3	44.7
0.5	5.0	22.0	45.5
0.5	6.66	21.6	46.4
0.5	8.33	21.3	47.2
0.5	10.0	20.9	48.2

Watch glass No. 1 of the second series when calculated to the same T_0 as watch glass No. 1 of the first series gave an activity of 44.6. The natural fall of the electroscope during these measurements was 0.7 scale division per minute, which has been taken into consideration in the "Corrected Activity."

Three-tenths of a gram of thallium iodide with 6.6 millimoles of potassium bromide per liter were used. All experiments were run in triplicate. The first set was run for 15 minutes at 1500 r.p.m. and there was found to be a 30.1 per cent adsorption. The second set was run for 30 minutes at 2500 r.p.m. and there was found to be an adsorption of 31.2 per cent.

3. *The effect of hydrogen-ion concentration on the adsorption of thorium B by thallium iodide*

The results of this study are given in table 2 and plotted in the curve given in figure 3. The results seem to indicate that an acid concentration

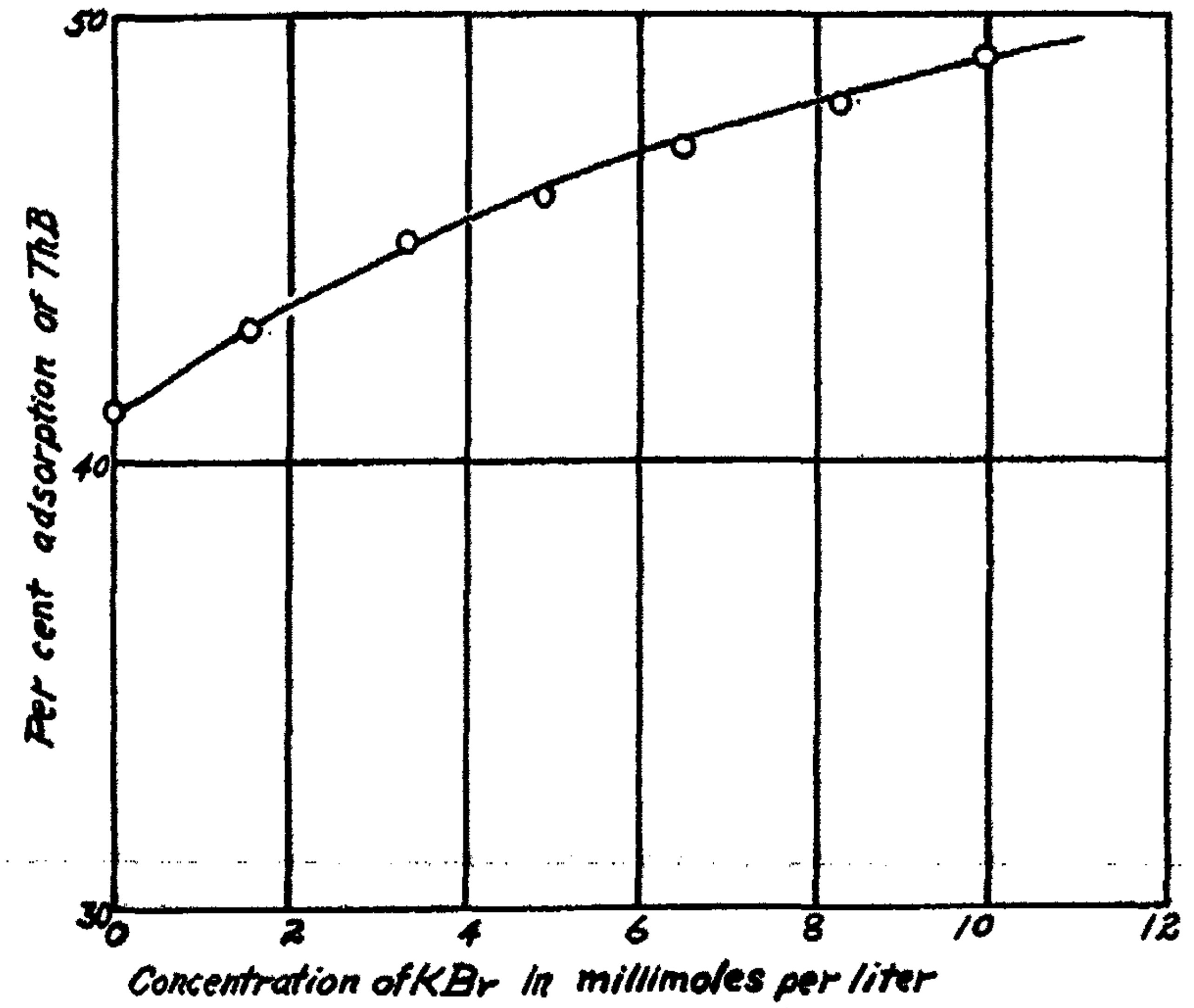

FIG. 2. ADSORPTION OF THORIUM B ON THALLIUM BROMIDE IN THE PRESENCE OF EXCESS BROMIDE IONS

TABLE 2

Effect of hydrogen-ion concentration on the adsorption of thorium B by thallium iodide

0.3 g. of thallium iodide used in all measurements. Each measurement was made in duplicate and the average for the two measurements is given.

NITRIC ACID	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter	*scale divisions per minute*	*per cent*
1.6*	62.4	
1.6	31.6	49.4
2.0	32.1	48.6
2.33	33.4	46.5
2.66	33.4	46.5
3.00	34.2	45.2
3.33	34.5	44.8
3.66	35.2	43.6
6.0	35.3	41.1
7.0	35.5	40.8
8.0	36.4	39.3
9.0	36.2	39.6
10.0	36.3	39.4

* Control; no thallium iodide.

of 6 millimoles per liter is sufficient to eliminate the main part of the effects due to adsorption on the glass walls or due to the formation of the colloidal particles of the thorium B.

4. *The effect of excess iodide ion and excess thallium ion on the adsorption of thorium B by thallium iodide*

In this series of experiments 0.3 gram of thallium iodide was used and the nitric acid concentration of the solutions was 6 millimoles per liter. The results are given in table 3 and the data is plotted in the curve given in figure 4.

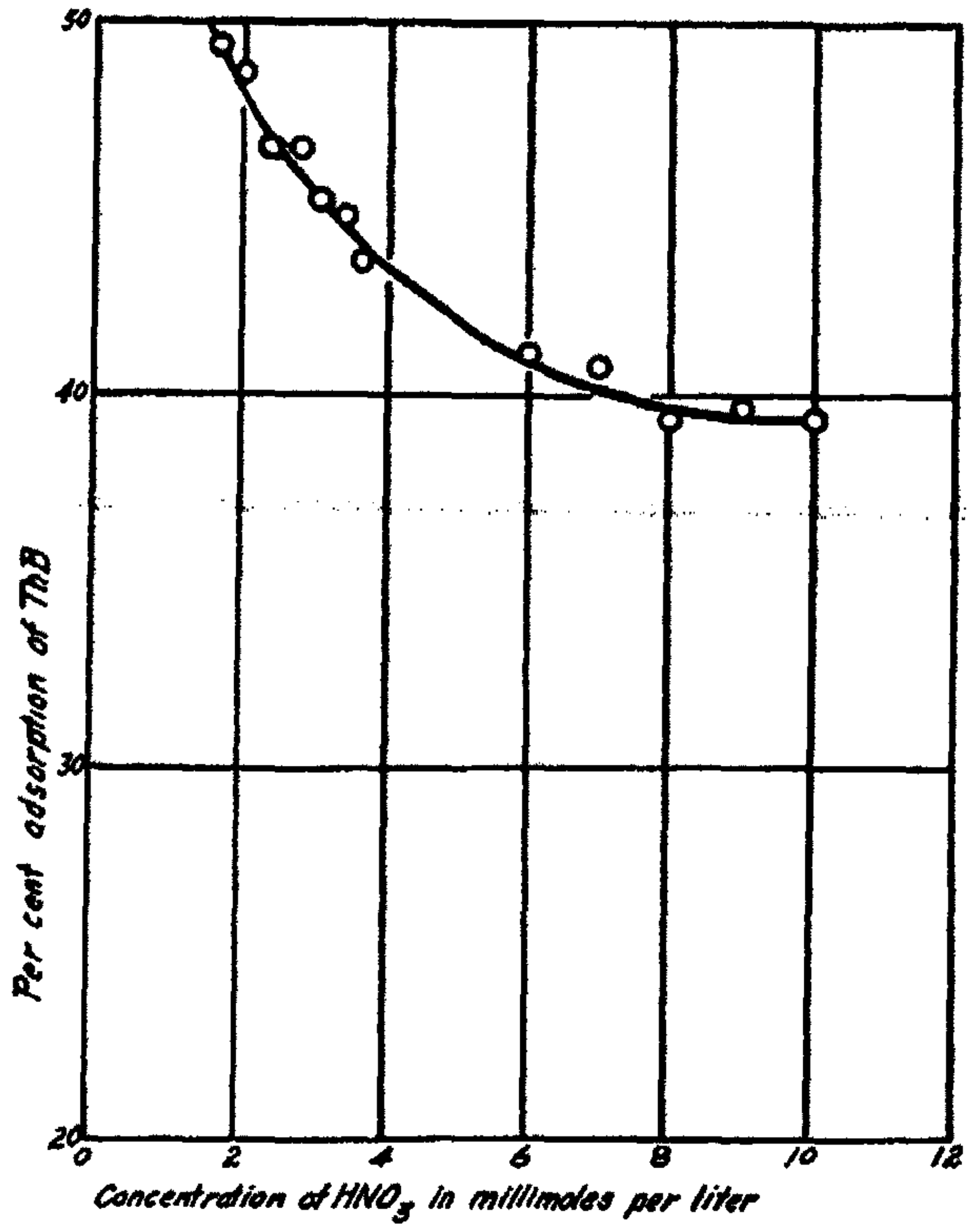

FIG. 3. ADSORPTION OF THORIUM B ON THALLIUM IODIDE WITH CHANGING HYDROGEN-ION CONCENTRATION

5. *Effect of an increase of the surface of the adsorbent on the amount of thorium B adsorbed*

In a duplicate series of runs 0.5 g. of thallium iodide in the presence of varying concentrations of excess potassium iodide was used. This data obtained is compared in curve I of figure 5 with that obtained in table 4 as given in curve II. It is to be realized that where the activity of a solution is removed to such an extent by the adsorbent as was the case in the greatest adsorption with 0.5 g. of thallium iodide the measurements on the residual activity of the solutions are of no great accuracy. The last point of curve I represents a measured activity (corrected) of 1.5 scale

TABLE 3

Effect of excess iodide ion and excess thallium ion

Concentration of nitric acid = 6 millimoles per liter
Adsorbent = 0.3 g. of thallium iodide

POTASSIUM IODIDE	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter	*scale divisions per minute*	*per cent*
0*	58.5	
0	39.4	32.7
0.55	19.7	66.4
1.1	10.2	82.6
1.66	7.1	87.9
3.33	3.9	92.2
8.3	1.4	97.6

THALLIUM NITRATE	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter	*scale divisions per minute*	*per cent*
0*	45	
0.66	37.5	16.6
1.34	40.1	10.9
2.00	41.4	8.0
2.66	42.2	6.3

[*] Control; no thallium iodide.

TABLE 4

Effect of excess bromide ion

Concentration of nitric acid = 6 millimoles per liter
Adsorbent = 0.3 g. of thallium iodide

POTASSIUM BROMIDE	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter	*scale divisions per minute*	*per cent*
0*	53.1	
0*	53.0	
0.833	34.9	34.3
0.833	34.5	35.1
1.66	34.9	34.3
3.33	35.0	34.1
3.33	34.4	35.2
5.00	34.4	35.2

[*] No thallium iodide.

divisions per minute when the natural fall of the electroscope was 0.8 scale divisions per minute. In all the work in this paper, at least two samples of each solution were taken for analysis. Therefore to obtain the figure for an

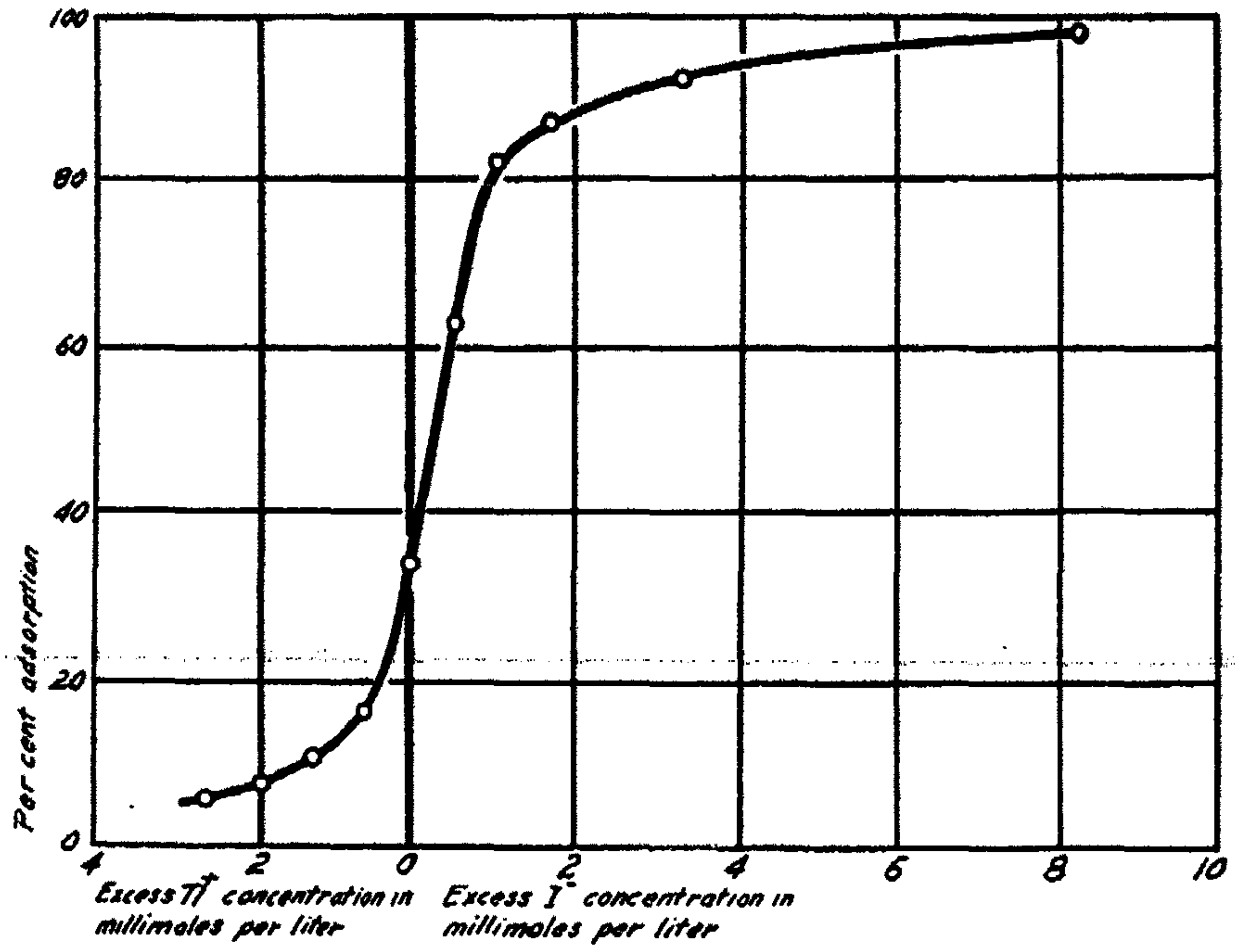

FIG. 4. ADSORPTION OF THORIUM B ON THALLIUM IODIDE WITH EXCESS THALLIUM IONS AND IODIDE IONS

TABLE 5

Effect of chloride ion on the adsorption

Concentration of nitric acid = 6 millimoles per liter
Adsorbent = 0.3 g. of thallium iodide

POTASSIUM CHLORIDE	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter	*scale divisions per minute*	*per cent*
0*	49.9	
0.833	34.6	30.7
0.833	34.5	30.9
1.66	34.8	30.4
1.66	35.0	29.8
3.33	35.4	29.1
3.33	35.5	28.9
5.0	35.7	28.5
5.0	36.0	27.9

* Control; no thallium iodide.

average adsorption of 97.8 per cent (the last point on the curve), four measurements were made on two different solutions with two different samples of 0.5 g. of thallium iodide.

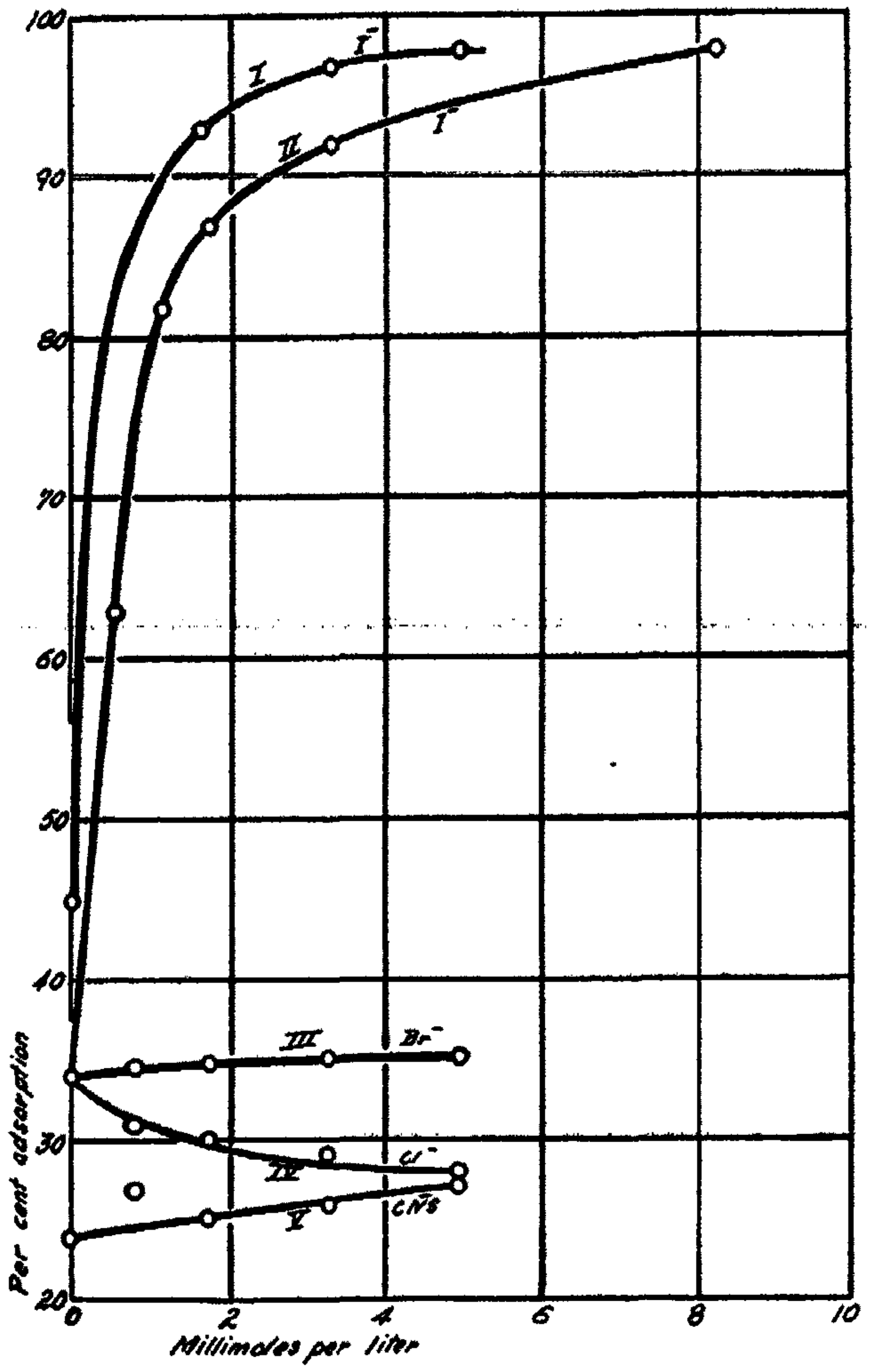

Fig. 5. Adsorption of Thorium B on Thallium Iodide in the Presence of Various Anions

6. *Effect of bromide ion on the adsorption*

Using a thallium iodide crystal powder which had an adsorption of 33.8 per cent, excess bromide ion was added. The results of this experiment are given in table 4 and plotted in figure 5.

7. *Effect of chloride ion on the adsorption*

In table 5 are given the results using chloride ion in place of bromide ion. The "neutral powder" used had an adsorption of 33.8 per cent. The data are plotted in the curve in figure 5.

TABLE 6

Effect of thiocyanate ions on the adsorption

Concentration of nitric acid = 6 millimoles per liter

Adsorbent = 0.3 g. of thallium iodide

POTASSIUM THIOCYANATE	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter	*scale divisions per minute*	*per cent*
0*	70.9	
0*	70.9	
0.833	51.9	26.8
0.833	49.4	30.3†
1.66	53.1	25.0
1.66	50.0	29.4†
3.33	52.3	26.2
3.33	52.3	26.2
5.00	51.5	27.3
5.00	51.6	27.4

* Control; no thallium iodide.

† These results were discarded because of difficulties encountered in the evaporation of the active solutions on the watch glasses. Owing to some cause the residue salts were unevenly distributed over the watch glasses.

TABLE 7

Effect of chromate ions from potassium chromate on the adsorption

Concentration of nitric acid = 6 millimoles per liter

Adsorbent = 0.3 g. of thallium iodide

POTASSIUM CHROMATE	pH OF SOLUTION	CORRECTED ACTIVITY	ADSORPTION	
millimoles per liter		*scale divisions per minute*	*per cent*	
0*	2.04	36.0		
0.83	2.31	23.0	36.2	
0.83	2.31	22.1	38.6	37.4
1.67	3.80	13.1	63.6	
1.67	3.80	15.9	55.9	59.9
3.33	5.23	4.3	88.0	
3.33	5.23	3.3	90.8	89.4
5.0	—	2.2	93.9	
5.0	—	1.8	95.0	94.5

* Control; no thallium iodide.

8. Effect of thiocyanate ion on the adsorption

The results of the measurements made using excess of thiocyanate ion are given in table 6 and plotted in figure 5. The crystal powder used in this series of measurements had an adsorption of 24.2 per cent.

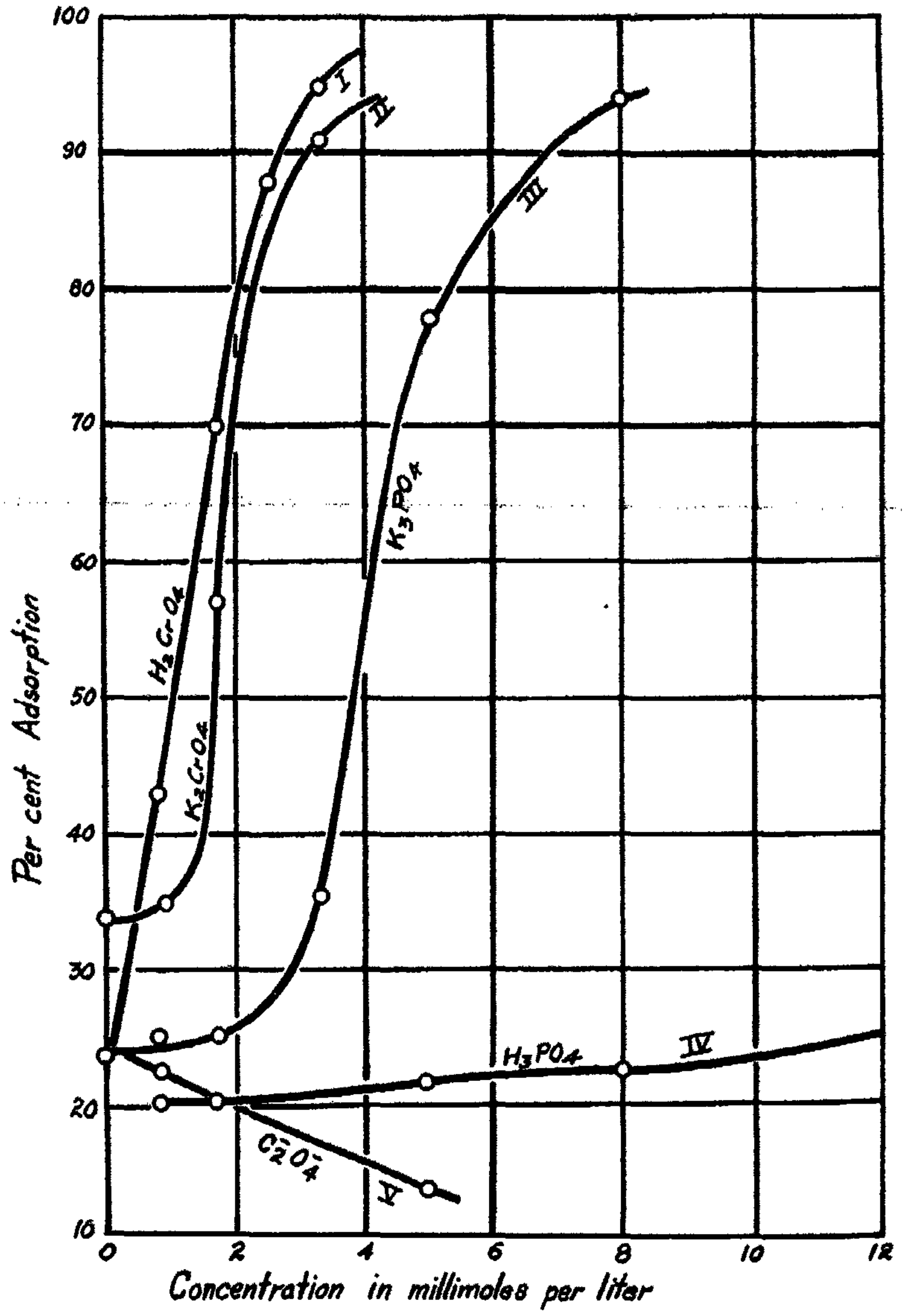

FIG. 6. ADSORPTION OF THORIUM B ON THALLIUM IODIDE IN THE PRESENCE OF VARIOUS IONS

9. *Effect of chromate ions on the adsorption*

The same experiments were carried out using excess chromate ions. In the first series of measurements, potassium chromate was used as a source of CrO_4^{--} ions. Since this introduced the complication of the hydrolysis of the potassium chromate with the resulting neutralization of the 6 millimoles

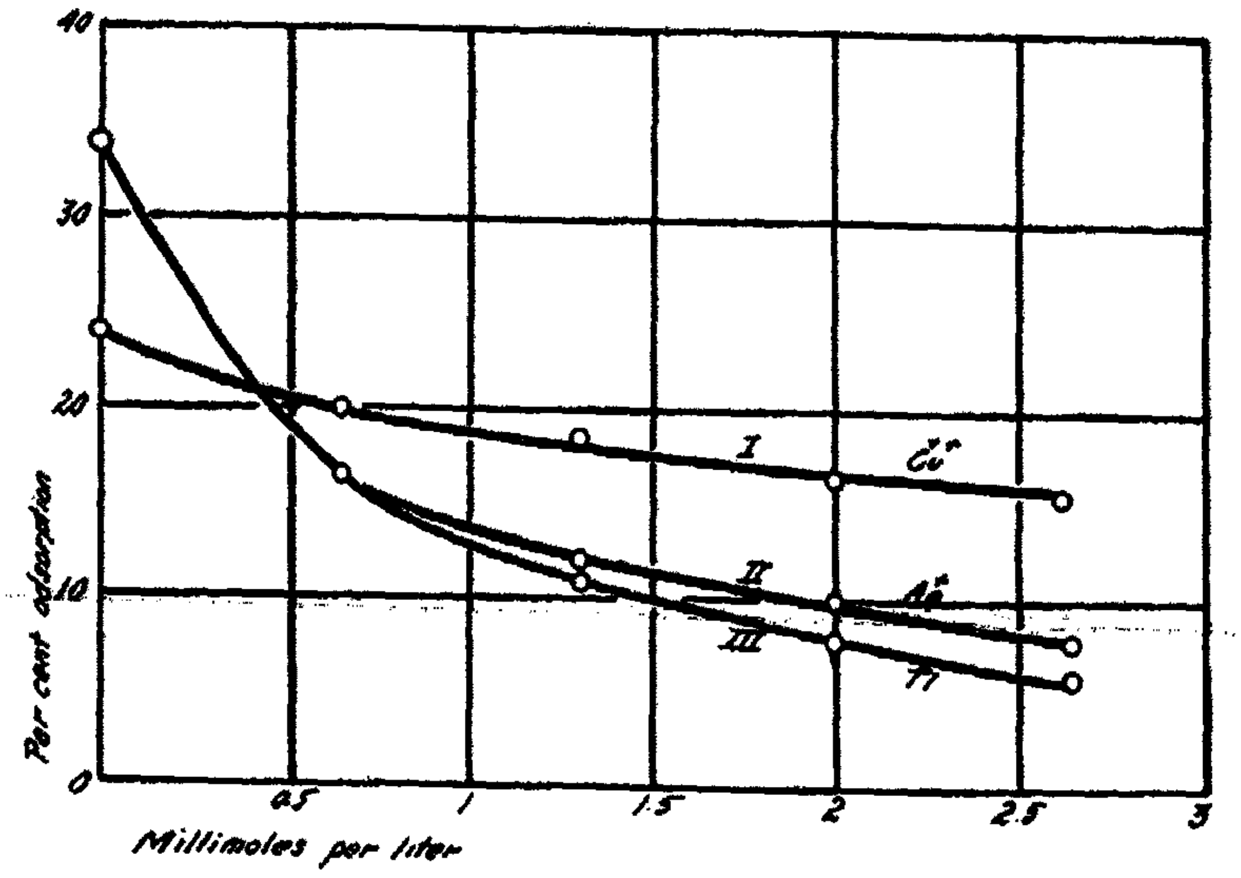

Fig. 7. Adsorption of Thorium B on Thallium Iodide in the Presence of Excess of Various Cations

TABLE 8

Effect of chromate ions from chromic acid on the adsorption

Enough nitric acid was added to bring the H+ ion concentration up to that recorded in the pH column

Adsorbent = 0.3 g. of thallium iodide

CHROMIC ACID	pH	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter		*scale divisions per minute*	*per cent*
0*		67.4	
0*		67.6	
0	2.6	54.5	19.4
0	2.6	55.4	19.3
0.833	2.6	38.2	43.5
1.66	2.6	20.4	69.9
1.66	2.6	20.0	70.5
2.5	2.7	8.7	87.2
2.5	2.7	8.1	88.1
3.33	2.7	3.3	95.2
3.33	2.7	3.3	95.2

Control; no thallium iodide.

per liter of nitric acid which was necessary in the solution to obtain reproducible results, another series of experiments was run using chromic acid as a source of chromate ions. An attempt was made to reduce the amount

TABLE 9

Effect of phosphate ions from potassium phosphate on the adsorption

Concentration of nitric acid = 6 millimoles per liter

Adsorbent = 0.3 g. of thallium iodide which had an adsorption of 24.2 per cent

POTASSIUM PHOSPHATE	pH	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter		*scale divisions per minute*	*per cent*
0*	2.04	30.1	
0.83	2.24	22.6	25.0
1.67	2.38	22.8	24.3
1.67	2.38	22.6	25.0
3.33	5.39	19.3	36.0
3.33	5.39	19.6	35.0
5.0	7.10	6.5	78.4
5.0	7.10	7.0	76.8
8.0	—	3.0	94.0

* Control; no thallium iodide.

TABLE 10

Effect of phosphate ions from phosphoric acid on the adsorption

Enough nitric acid was used to make the total H^+ ion concentration equal to that indicated in the column of pH measurements

Adsorbent = 0.3 g. of thallium iodide

PHOSPHORIC ACID	pH	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter		*scale divisions per minute*	*per cent*
0*	—	67.4	
0*	—	67.6	
0.83	2.29	54.2	19.9
1.67	2.36	53.7	20.6
1.67	2.36	54.5	19.4
5.0	2.28	53.0	21.6
5.0	2.28	52.8	21.9
8.0	2.29	52.0	23.1
8.0	2.29	52.5	22.4
16.7	2.22	45.9	32.2
16.7	2.22	47.3	30.4
16.7†	—	65.4	3.0
16.7†		65.0	3.6

* Control; no thallium iodide.

† No thallium iodide.

From the last two measurements there is an average "holding back" effect, due to the phosphoric acid, of some 3.3 per cent. This would make the corrected adsorption for the 10th and 11th measurements 28.0 per cent.

of nitric acid in the solution as the amount of chromic acid increased in order to keep the hydrogen-ion concentration constant. pH measurements were made on the solutions after the adsorption equilibrium had been reached, using the quinhydrone electrode. In the case of chromic acid it was difficult to obtain consistent results with this electrode because of the oxidizing action of the chromic acid. However, by using the voltage recorded at the beginning, fairly consistent results were obtained, which indicated that the acid concentration was sufficiently constant. The results are given in tables 7 and 8 and the data is plotted in the curves in figure 6.

TABLE 11

Effect of oxalate ions on the adsorption

Concentration of nitric acid = 6 millimoles per liter

Adsorbent = 0.3 g. of thallium iodide which had an adsorption of 24.2 per cent

POTASSIUM OXALATE	pH	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter		*scale divisions per minute*	*per cent*
0*	2.04	32.9	
0.83	2.13	25.4	22.8
0.83	2.13	25.8	21.6
1.67	2.16	26.2	20.3
1.67	2.16	26.3	20.3
5.0	2.46	28.7	12.8
5.0	2.46	28.2	14.2

* Control; no thallium iodide.

TABLE 12

Effect of silver ions on the adsorption

Concentration of nitric acid = 6 millimoles per liter

Adsorbent = 0.3 g. of thallium iodide with an adsorption of 33.8 per cent

SILVER NITRATE	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter	*scale divisions per minute*	*per cent*
0*	76.3	
0.66	64.1	16.0
0.66	63.1	17.3
1.34	67.0	12.2
1.34	67.7	11.3
2.00	69.2	9.3
2.00	68.0	10.9
2.66	69.5	8.9
2.66	70.3	7.9

* Control; no thallium iodide.

10. Effect of phosphate ion on the adsorption

Because of the hydrolysis of the potassium phosphate used, with the resultant neutralization of the nitric acid in the solution, a second series was run using phosphoric acid as the source of the PO_4^{---} ion. In tables 9 and 10 are given the results of the experiments with excess phosphate ions and the pH measurements of the solutions. The results are plotted in figure 6.

TABLE 13

Effect of cupric ions on the adsorption

Concentration of nitric acid = 6 millimoles per liter
Adsorbent = 0.3 g. of thallium iodide with an adsorption of 24.2 per cent

CUPRIC NITRATE	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter	*scale divisions per minute*	*per cent*
0*	73.9	
0.67	59.5	19.4
0.67	58.5	20.8
1.33	60.4	18.5
2.0	61.6	16.6
2.67	62.7	15.2
2.67	61.6	16.6

* Control; no thallium iodide.

TABLE 14

Effect of lead ions on the adsorption

Concentration of nitric acid = 6 millimoles per liter
Adsorbent = 0.3 g. of thallium iodide with an adsorption of 33.8 per cent

LEAD NITRATE	CORRECTED ACTIVITY	ADSORPTION
millimoles × 10^{-3} per liter	*scale divisions per minute*	*per cent*
0*	46.2	
0.163	31.0	32.9
0.163	31.2	32.5
1.63	32.1	30.6
16.3	40.8	11.7
16.3	41.3	10.7
32.6	42.3	8.5
32.6	43.0	7.0

* Control; no thallium iodide.

11. Effect of the oxalate ion on the adsorption

In table 11 are given the results of the experiments in which an excess of oxalate ion was used. These results are plotted in the curve in figure 6.

12. Effect of silver ion on the adsorption

In table 12 are given the results of the measurements of the adsorption in the presence of excess of silver ions. The results are plotted in the curve in figure 7.

13. The effect of cupric ions on the adsorption

In table 13 are given the results of the experiments carried out on the adsorption in the presence of excess cupric ions. These results are shown graphically in the curve in figure 7.

14. The effect of the lead ions on the adsorption

In table 14 are given the results of the measurements in which the adsorption was allowed to take place in the presence of small concentrations of lead ions.

DISCUSSION OF RESULTS

1. It is to be noted that in no case have we been able to prepare a "neutral powder" which had no adsorption for thorium B ions (5). In all the experiments the concentration of the thorium B was kept constant as described on page 854 because work of King and Greene (6) will show that there is a slight difference in the amount of activity adsorbed from solutions of varying activity. In experiment 1 with thallium bromide as the adsorbent, as much as 10 millimoles per liter of potassium bromide caused an increase in the adsorption of only some 8 per cent. We found that with this amount of excess potassium bromide there was no measurable "holding back" effect. This small increase in adsorption can be explained by the relatively high solubility of the thallium bromide, 1.7 millimoles per liter.

2. Experiment 2 shows that centrifuging the samples at 1500 r.p.m. for ½ hour is sufficient to remove any fine particles of powder from the solution which might have adsorbed thorium B ions and caused an apparent larger activity of the supernatant solution used for analysis.

3. Experiment 3 is concerned with one of the most interesting phases of the whole problem, namely, the question of the physical condition of the radioactive material in the solution, which has been discussed in the paper by King and Romer (1). In addition to the possibilities of "pseudo colloids," "radiocolloids," hydrolyzed particles of thorium B and thorium C and the charge on the walls of the glass vessels, all of which are affected by the amount of hydrogen ion, there is also the possibility of the competition of hydrogen ion with thorium B ions for a place on the surface of the crystals. This was brought out in the paper of Fajans and Erdey-Grúz who found that there was a large decrease in the amount of thorium B adsorbed on several silver salts when the acid concentration of the acid in the solution increased from 0.004 normal to 0.05 normal.

4. Experiment 4 shows the effect of increasing the minus charge on the thallium iodide crystals by the addition of iodide ions and that of decreasing the minus charge by the addition of thallium ions. The adsorption phenomenon is continuous, as shown by the curve in figure 4. With an excess of 2.7 millimoles of thallium nitrate per liter, there is still an adsorption of some 6 per cent. This does not necessarily mean that the thallium iodide crystals are still negatively charged. Lange and Crane (2) found silver iodide crystals neutral at a silver ion concentration of 1×10^{-6}. Fajans has shown by electroendosmosis experiments that thorium B ions can be adsorbed on silver salt particles which are positively charged.

5. In experiment 5 no direct determination was made of the magnitude of the surface of the thallium halide crystals used. From repeated tests the surface per gram remained constant for the purposes of our experiments. The same preparation of thallium halide salt was used for each series of measurements. Experiment 5 shows the increase in the adsorption caused by an increase in surface of that of 0.3 g. to that of 0.5 g. J. Walker estimated the surface of his silver bromide by microscopic method to be 2×10^3 sq. cm. per gram.

6. Experiments 6, 7, and 8. From observation of figure 8 it can be seen that the effect of the anions on the adsorption is in the order

$$I^- > CNS^- > Br^- > Cl^- .$$

It is to be noted that not all measurements were made on the same sample of powder.

The differences in the amounts of adsorption of thorium B by two different preparations of "neutral powder" can be attributed to the differences in the surface per gram of the different powders and also the difference in the numbers of points on the crystals to which are attached halide ion (i.e., the charge on the particles). The change in the adsorption due to the addition of an electrolyte represents the ability of the electrolyte to increase the charge on the crystal, that is, to add a further excess of anions to the crystal. Therefore we are able to compare the effect of two different anions on two different preparations of powders. For instance, 3.3 millimoles per liter of excess potassium bromide on one powder caused an increase in the adsorption of thorium B of 0.9 per cent, while the same amount of excess potassium thiocyanate on another preparation caused an increase in the adsorption of 2 per cent.

If results obtained using an excess of the salt of 3.3 millimoles per liter are taken for comparison, we find for

I^- an increase of 58 per cent in adsorption
CNS^- an increase of 2 per cent in adsorption
Br^- an increase of 0.9 per cent in adsorption
Cl^- a decrease of 5 per cent in adsorption

Fajans found this same order for the ions in his study of the displacement of erythrosinate ion from the surface of silver iodide. From the solubility table given on page 873 it is seen that thallium thiocyanate is more soluble than thallium bromide. In other words, the thiocyanate ion is out of order on a strict solubility consideration because thiocyanate ions are better adsorbed than are bromide ions. Fajans showed the same to be true in the case of the adsorption of thorium C on silver sulfide. The adsorption rule which states that adsorbability is related to insolubility is to be applied to similar or analogous ions. The order of adsorbability and insolubility holds good for the halide ions. In the case of the large organic dye ions—eosinate and erythrosinate—the rule also holds. Silver eosinate has a solubility of 5×10^{-5} moles per liter, while silver erythrosinate has a solubility of 1.1×10^{-6}; that is, silver eosinate is about fifty times as soluble as silver erythrosinate. On 1 g. of silver bromide in a solution 2×10^{-6} molar in erythrosinate ion, 15 per cent of the erythrosinate ions were adsorbed, but when 1 g. of silver bromide was brought to equilibrium in a solution of eosinate ion five times more concentrated only 5 per cent of the eosinate ions were adsorbed. When halide ions are compared with large organic dye ions, another determining factor enters. The halide ions were used to replace adsorbed erythrosinate ions from the surface of silver halides. It was shown that even though silver erythrosinate was more soluble than the silver halides, the erythrosinate ion was much more adsorbed. Therefore, in addition to the simple electrostatic attraction which exists between a large ion and the crystal surface, another factor due to the non-polar forces or semipolar forces (deformation effect) becomes significant. For this reason it can be expected that the large dissimilar thiocyanate ion is more readily adsorbed than the bromide ion even though thallium bromide is more insoluble than thallium thiocyanate.

7. An effect in experiments 7 and 11 (shown in the curves in figures 5 and 6) is to be noted. Here an excess of potassium chloride and potassium oxalate decreases the amount of adsorption. Addition of 5 millimoles of potassium chloride per liter causes some 6 per cent decrease, and addition of the same amount of potassium oxalate causes a decrease of some 11 per cent. Thallium chloride is soluble to the extent of 13 millimoles per liter, and thallium oxalate to the extent of 53 millimoles per liter. This high solubility should be accompanied by a slight tendency for chloride ion and oxalate ion to be adsorbed. Since all ions possess some tendency to become attached to the surface of a crystal lattice, we have here in this case an opportunity for potassium ions to be adsorbed along with thorium B ions (or potassium ions to decrease the charge on the crystal and thereby decrease the amount of thorium B adsorbed). In other words, a large concentration of potassium ions may replace from the surface some thorium B ions as did the hydrogen ions as discussed above. When Fajans used

potassium chloride to replace the erythrosinate ions from the surface of silver iodide, he found an increase of adsorption rather than a decrease. Further work on the adsorption of the alkali ions and the alkaline earth ions is to be reported in a subsequent paper.

8. Experiments 9 and 10 deal with work on adsorption in the presence of an excess of a hydrolyzable electrolyte. In curve III in figure 6 the apparent adsorption is mainly due to the neutralization of the nitric acid by the potassium hydroxide formed in the hydrolysis and the subsequent adsorption of a kind discussed in paragraph 3 (p. 870). In curve IV of the same figure the adsorption is due to the addition of an ion which does not form a very insoluble compound. In figure 6 where hydrolysis takes place and also the anion forms an insoluble compound, curve I shows the increasing of the charge on the particles by the chromate ions and curve II shows an increasing of the charge and a neutralization of the acid.

TABLE 15

ION	PER CENT INCREASE IN ADSORPTION	SOLUBILITY
		millimoles per liter
I^-	58	0.18
*CrO_4^{--}	51	0.57
CNS^-	2	12.0
Br^-	1.9	1.7
*PO_4^{---}	0.0	7.0
Cl^-	−5.0	13.0
*$C_2O_4^{--}$	−4.0+ but decreasing more rapidly than Cl^-	53.0

* Milliequivalents per liter.

9. In table 15 the ions are listed in the order of their adsorbability on thallium iodide; also the per cent increase in the adsorption for 3.3 millimoles per liter of the electrolyte and the solubilities of the thallium salts are given. The order of adsorbability runs parallel with that of insolubility if the exception discussed above is made for thiocyanate ion.

10. In experiments 12, 13, and 14 it is shown that a cation which forms an insoluble salt with the anion of the crystal is adsorbed and will replace thorium B ions from the surface. In figure 7 are plotted the results for copper, silver, and thallium ions. Because copper iodide is more soluble than silver iodide, the copper ions do not replace thorium B as well as silver ions do. Silver iodide is less soluble than thallium iodide, but thallium ions are better adsorbed than silver ions, because in this case the thallium ions fit better into the crystal lattice than do silver ions. Lead ions and thorium B ions are equally well adsorbed by the crystals.

SUMMARY

1. A report has been given of a series of experiments carried out to determine the effect of various anions and cations on the adsorption of thorium B ions on thallium bromide and thallium iodide crystals.

2. The purest thallium bromide and thallium iodide which could be prepared showed a negative charge and adsorbed thorium B ions.

3. The adsorption rule which postulates that the insolubility of the salt formed by the ion being adsorbed with the oppositely charged ion of the crystal determines the adsorbability of the ion has been verified for I^-, CrO_4^{--}, CNS^-, Br^-, PO_4^{---}, Cl^-, $C_2O_4^{--}$ ions on thallium iodide crystals.

4. The ionic deformation theory has been used to explain the relative adsorbability of the halide ions and the thiocyanate ion.

5. The question of the effect of hydrogen ion on the adsorption of thorium B on thallium iodide has been discussed.

6. Results have been reported on the measurements made of the effect of Ag^+, Cu^{++}, Tl^+, and Pb^{++} on the adsorption of thorium B on thallium iodide crystals.

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THE ABSORPTION SPECTRA OF A SERIES OF ORGANIC MOLECULAR COMPOUNDS[1]

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Pfeiffer (1) and others have investigated the colored molecular compounds resulting from quinones with aromatic hydrocarbons, ethers, or amines. Pfeiffer has classified these compounds with the quinhydrones and has shown that a series extends from the intensely colored quinhydrones existing as crystalline compounds, through colored complexes difficult to crystallize, to complexes impossible to crystallize and identified largely by a slight color change on mixing the liquid components. These latter "molecular compounds" are tied by forces which are weak in comparison with the intermolecular forces in the crystals of the components, for, on cooling, the components of the mixture crystallize out separately. Foreign solvents tend to dissociate the compounds and as a result Beer's law does not hold.

We undertook a spectroscopic study of the more weakly tied compounds of this type in the hope of extending the series of molecular compounds to loosely tied complexes which had escaped detection because the color change occurred in the ultra-violet or was too slight to be seen with the eye. There was also the possibility that the "solvent effect" of absorption spectroscopy could be linked with these color changes. Foremost, however, there was the hope that a correlation between color and oxidation-reduction potentials might be established.

RESULTS

We have carried out quantitative light absorption measurements on the five quinones—chloroquinone, benzoquinone, toluquinone, xyloquinone, and duroquinone—in a melted state and in the absence of any solvent. The resulting curves are compared with the light absorption of equimolecular mixtures of these quinones with various aromatic ethers, hydrocarbons, and

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[1] This article is based upon the thesis of E. H. Northey submitted to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, July, 1930. The manuscript was prepared by the junior author after the death of Dr. Hunter in 1931.—L. I. Smith.

[2] du Pont Fellow in Chemistry, 1929–1930.

amines. Thirty-three such combinations were investigated. No third component was used as solvent because of the probable dissociation it would involve; instead a thin layer of the liquid mixture was employed, necessitating the use of special absorption cells and technique. However, it is convenient to refer to the nonquinoid component of the equimolecular mixture as "solvent." This will be done in the subsequent discussion.

Practical considerations limited our choice of components. Melting points and vapor pressures of the pair had to be nearly equal, otherwise changes in composition occurred during measurement. Thus di-, tri- and tetra-chloroquinones were eliminated on account of their high melting points, and benzene, toluene, and hexamethylbenzene were eliminated on account of their high vapor pressures.

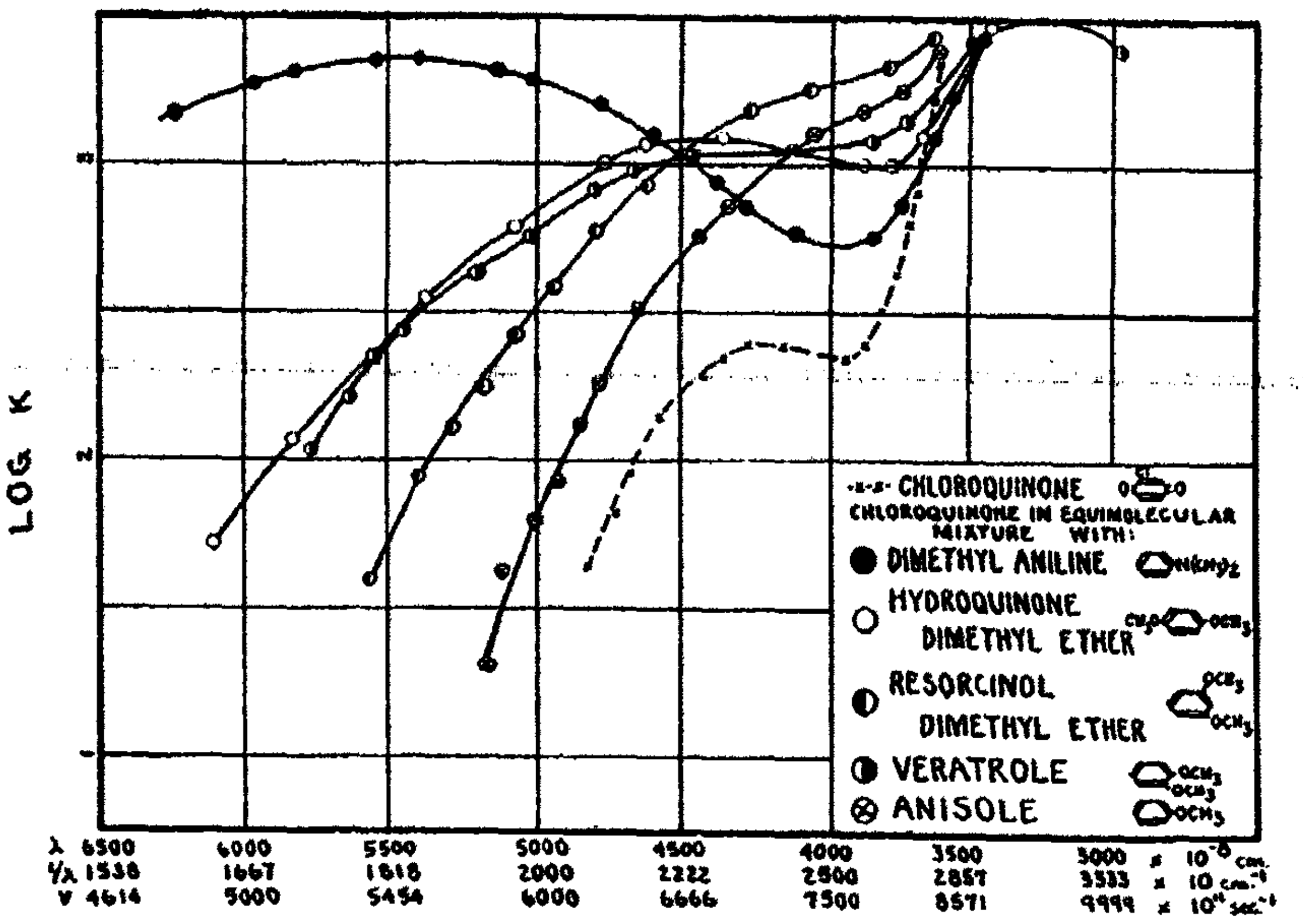

FIG. 1. CHLOROQUINONE

The results as shown in figures 1 to 7 are expressed in terms of the extinction coefficient as defined by the Bunsen-Roscoe law:

$$K = \frac{1}{d} \log_{10} \frac{I_0}{I}$$

where d is the thickness of absorbing layer in centimeters. These curves compare the absorption of a quinone with the absorption of its molecular compounds with various "solvents," assuming complete combination. Actually an equilibrium mixture was undoubtedly present and account

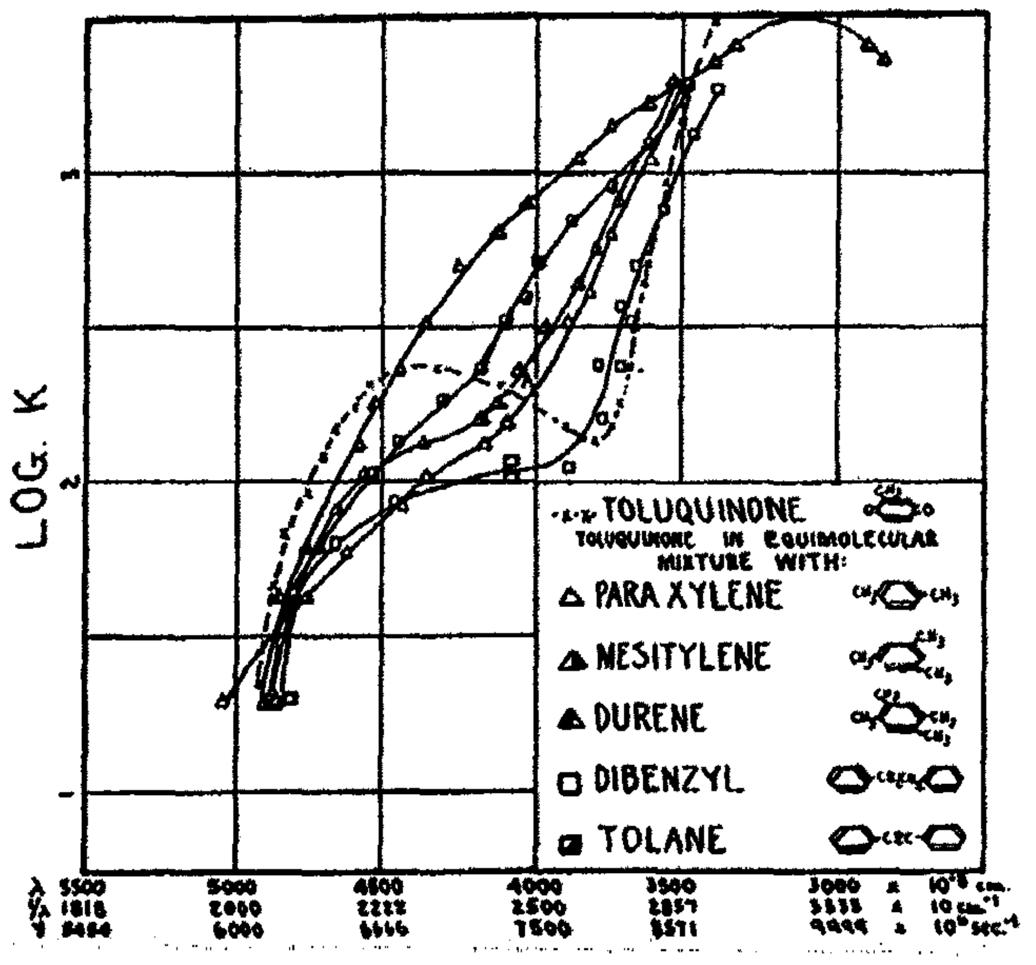

FIG. 2. CHLOROQUINONE

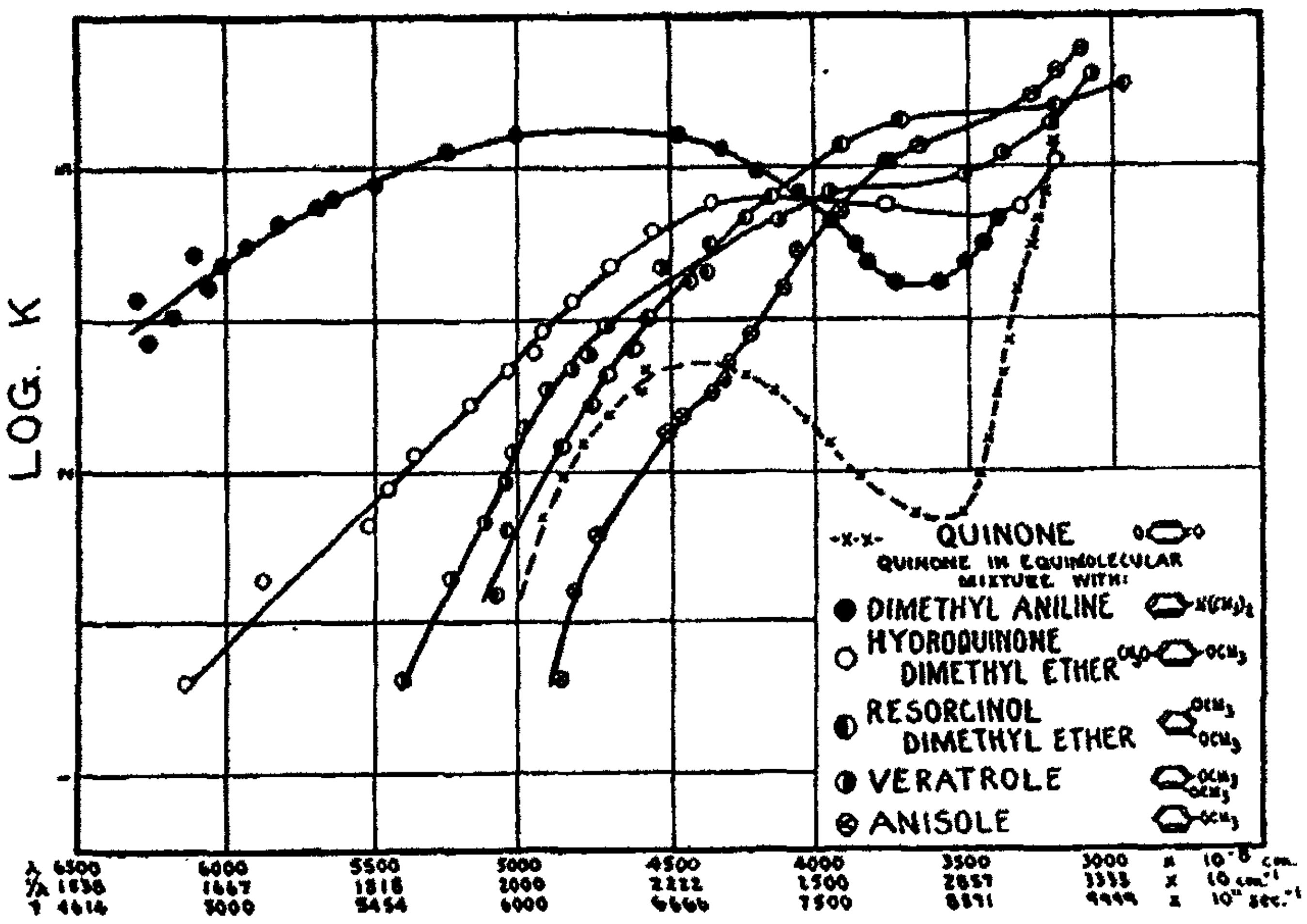

FIG. 3. QUINONE

should be taken of the absorption of uncombined quinone,[3] but since the dissociation constants were lacking, no correction could be made. However,

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[3] The solvents are nearly transparent in the region studied and their slight absorption was corrected for during measurement.

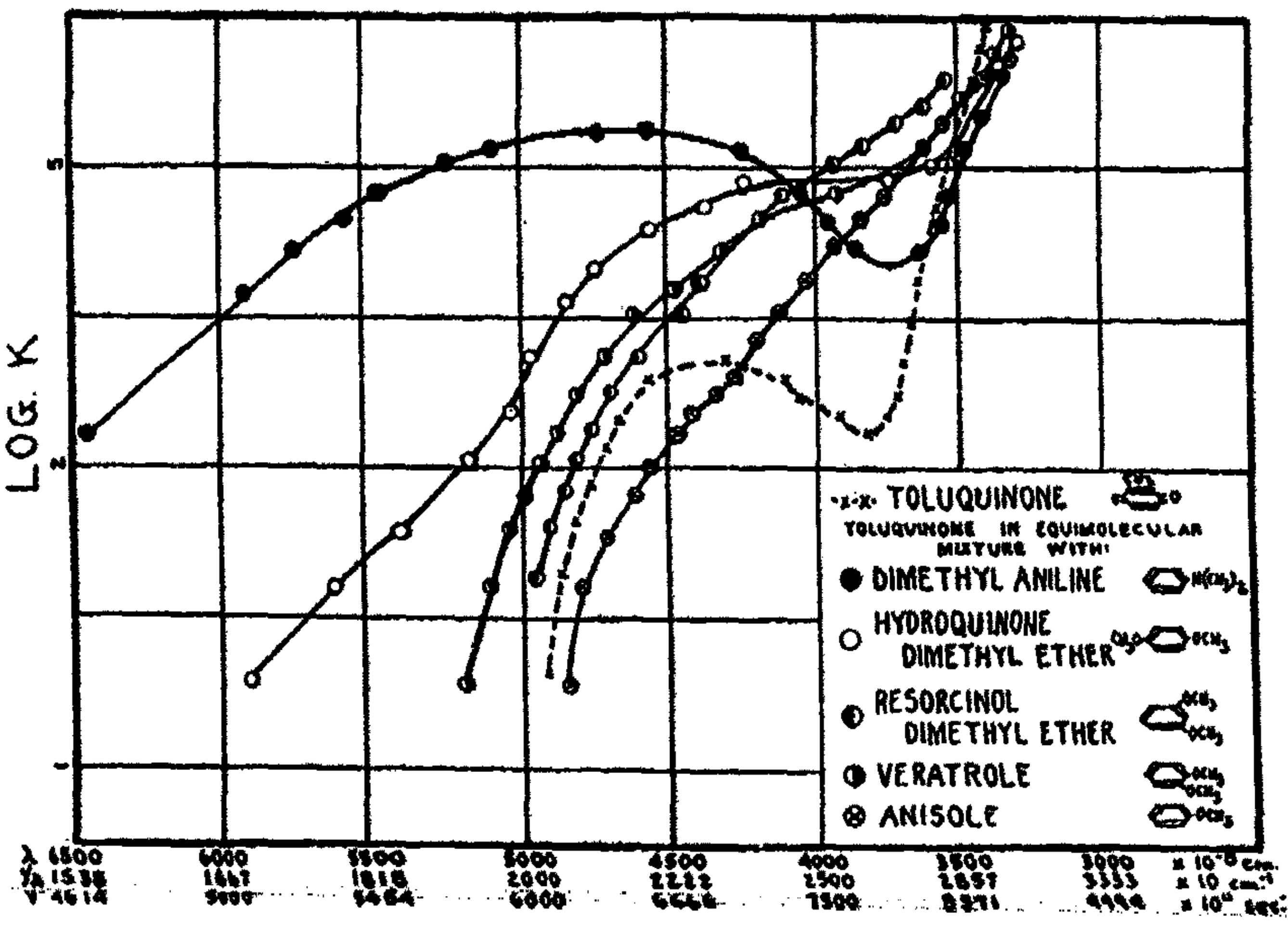

Fig. 4. Toluquinone

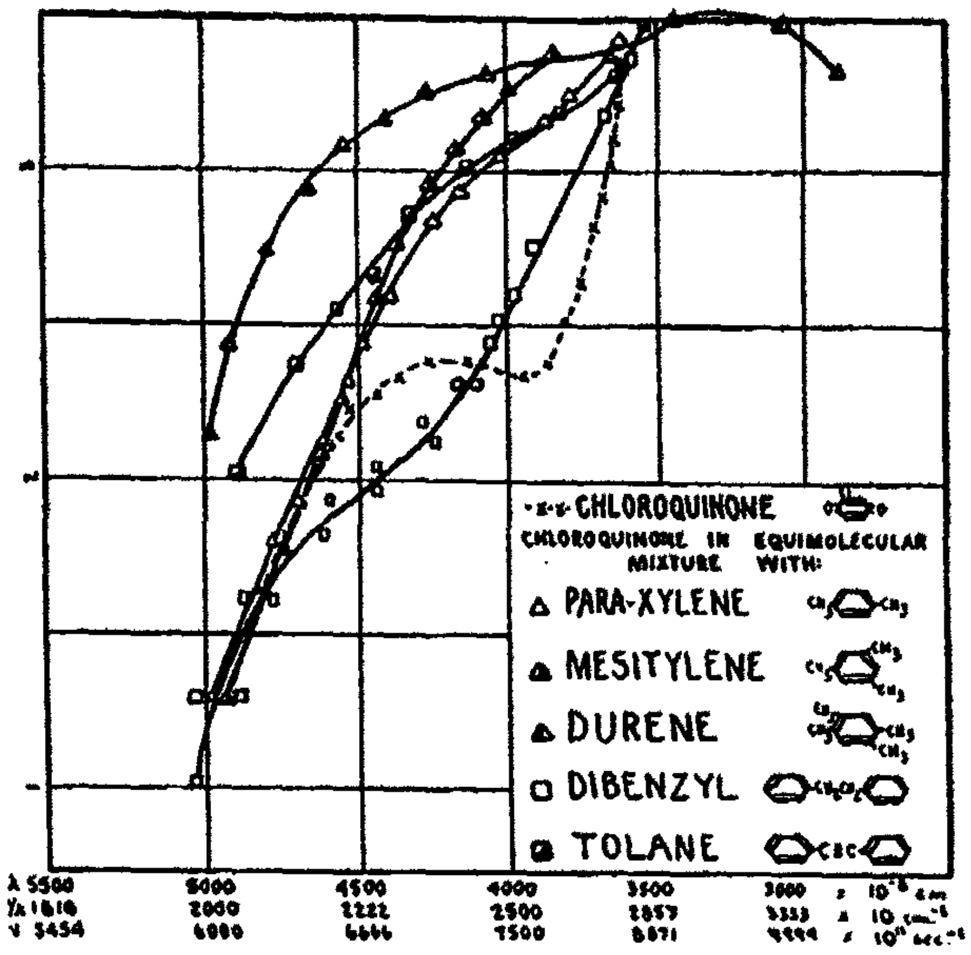

Fig. 5. Toluquinone

it was of considerable interest to replot the data on the assumption of no compound formation, i.e., it was assumed that the only effect of the "solvent" was simple dilution, and by calculating back to the absorption of quinone with solvent removed, curves were obtained which show the "sol-

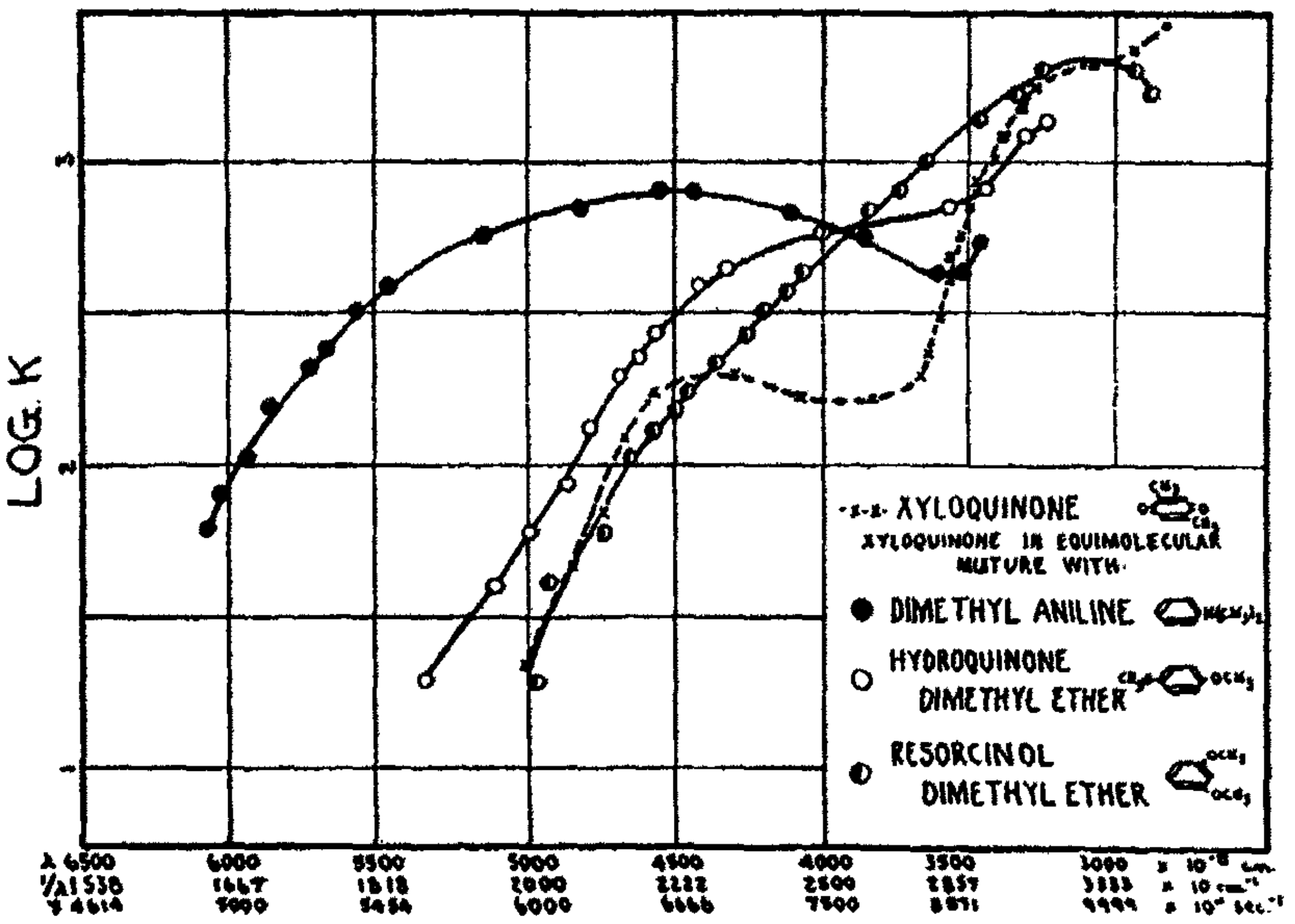

Fig. 6. Xyloquinone

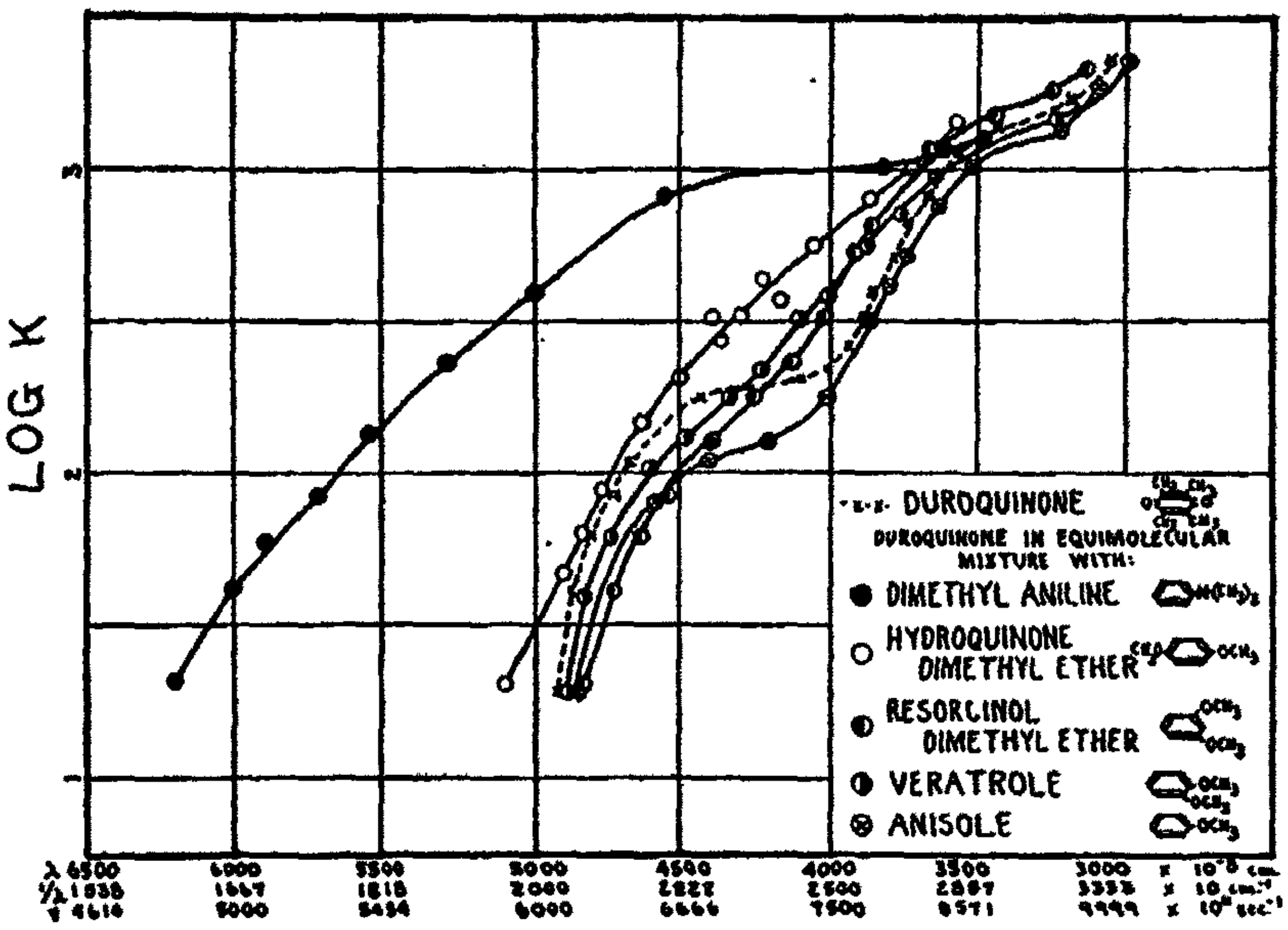

Fig. 7. Duroquinone

vent effect" to better advantage. Calculated in this way, and granting the assumptions, the absorption curves of a pure quinone and its various "solutions" should be identical.

Let K = the measured extinction coefficient of a quinone in solution, and K' = the extinction coefficient with solvent removed. K' will differ from K only in the thickness of the absorbing layer if the solvent is transparent and otherwise inert. The relationship is:

$$K' = \left[1 + r\frac{M_sS_q}{M_qS_s}\right]K$$

or

$$\log K' = \log K + C$$

where

$$C = \log\left[1 + r\frac{M_sS_q}{M_qS_s}\right]$$

TABLE 1

Values of C for equimolecular mixtures of quinone and "solvent"

	CHLORO-QUINONE	QUINONE	TOLU-QUINONE	DURO-QUINONE
Dimethylaniline	0.35	0.41	0.33	0.25
Hydroquinone dimethyl ether	0.36	0.42	0.34	0.26
Resorcinol dimethyl ether	0.36	0.42	0.34	0.26
Veratrole	0.35	0.41	0.33	0.25
Anisole	0.31	0.36	0.29	0.22
p-Xylene	0.34		0.32	
Mesitylene	0.37		0.35	
Durene	0.40		0.38	
Dibenzyl	0.38		0.36	

and M_s = molecular weight of "solvent,"
M_q = molecular weight of quinone,
S_s = density of "solvent,"
S_q = density of "quinone," and
r = mole ratio of "solvent" to "quinone."

Hence if $\log K$ is replotted as $\log K'$ the curve will simply be raised by an amount equal to C.

Densities of "solvent" and quinone must be known slightly above the melting point to make use of the formula. Most of the data needed were found in the literature, but rough determinations had to be made on the quinones. These densities are: for chloroquinone, $d^{60°}$ 1.38; toluquinone, $d^{70°}$ 1.07; duroquinone, $d^{115°}$ 1.02. A value for quinone was found in the literature, while insufficient xyloquinone was available for a determination.

The calculated values of C are given in table 1.

DISCUSSION OF RESULTS

Figure 8 shows the data on duroquinone replotted in terms of log K'. It is apparent that there is an effect of "solvent" other than simple dilution, since the "solution" curves deviate from that of the pure quinone. In the case of anisole this deviation is relatively small and is comparable with changes in the absorption spectrum of any substance observed by changing from one solvent to another. The increased effect of veratrole is still of the order of solvent effects and would be so ascribed in the absence of other data. There can be little doubt, however, that if the solvent effect is met with in the case of duroquinone it is the result of the same influences causing color changes in the case of chloroquinone. Since Pfeiffer has demonstrated that these color changes are a part of molecular compound formation, it appears that we have bridged the gap between true molecular compounds and one type of solvent effect.

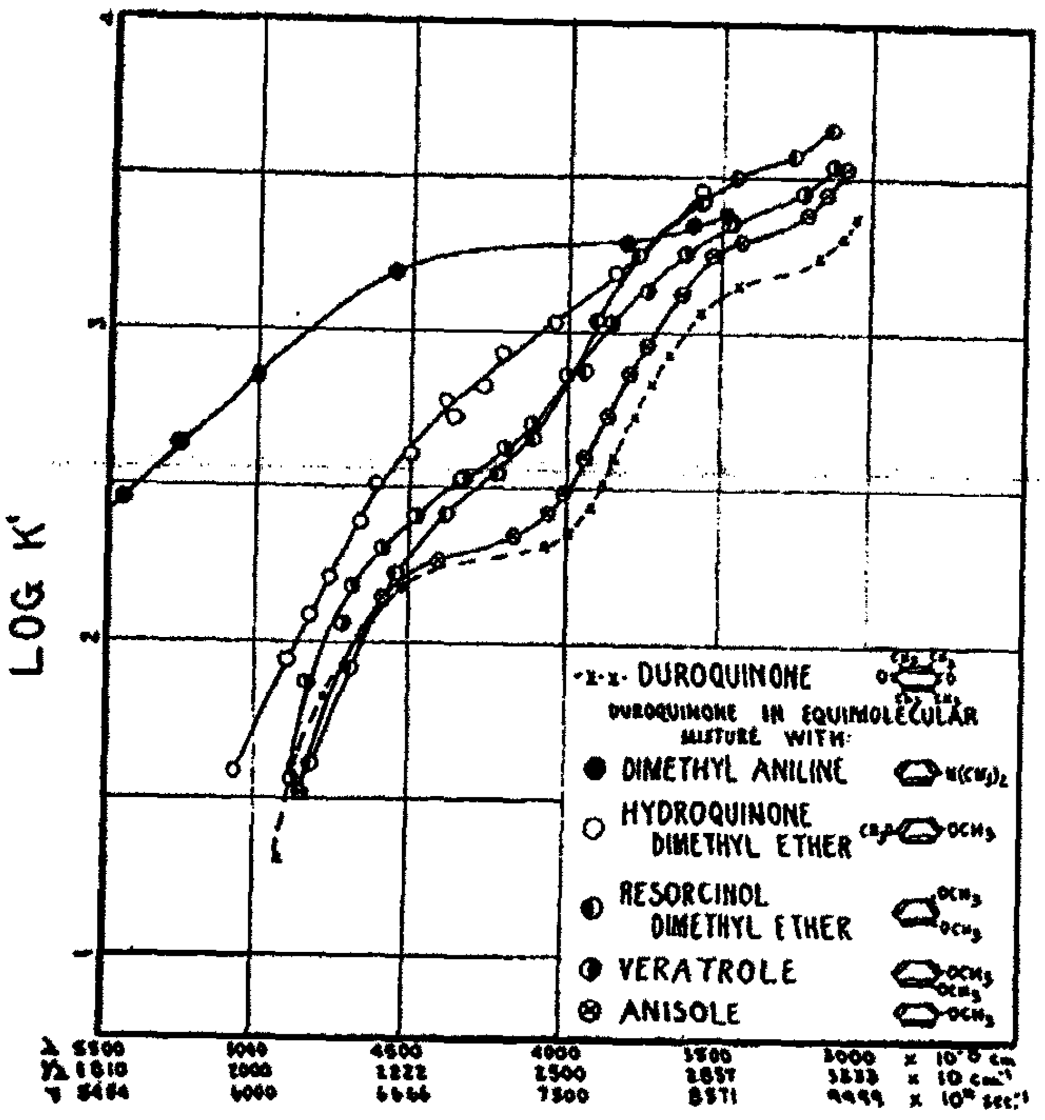

Fig. 8. Duroquinone

Comparison of figures 1 to 7 for any one "solvent" shows that the difference between the "solution" curve and quinone curve increases in the order duroquinone, xyloquinone, toluquinone, quinone, chloroquinone. In order to put these differences on a numerical basis we have arbitrarily measured the areas between the quinone curve, log $K = 1.5$, and the "solution" curves. The unit of area has no significance and the choice of log K at 1.5 was for convenience, as such choice does not affect the order of the results.

In figure 9 we have plotted these areas against Conant and Fieser's (2) values of π_0, the reduction potential in volts, of the respective quinones. Two generalizations can be drawn from these data:

I. In a series of quinones the change in the absorption spectrum, brought about by a solvent capable of forming molecular compounds, increases with increasing oxidation-reduction potential of the quinones.

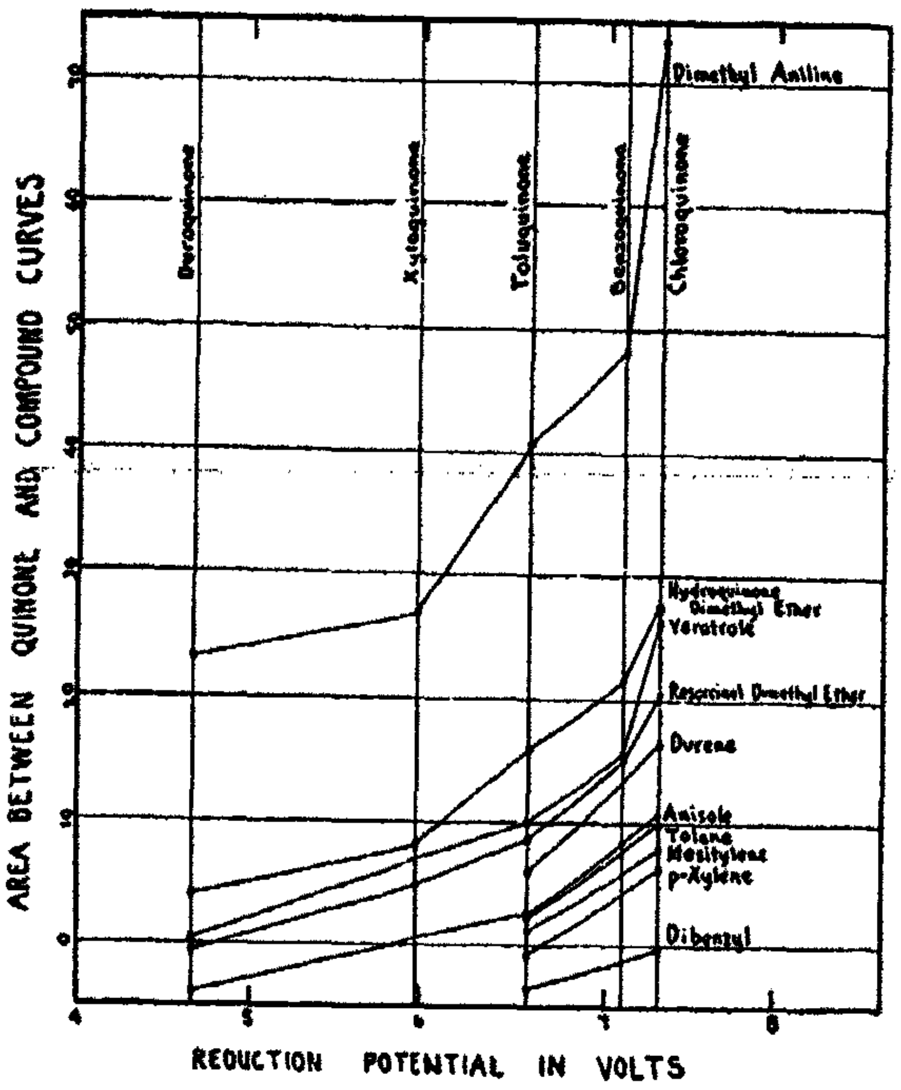

Fig. 9

II. The order in which "solvents" fall with respect to increasing effect on the absorption spectrum of a quinone is independent of the quinone studied.

The significance of these findings with respect to color theories is evident; however, additional experimental work along several lines is necessary in order to place the results here obtained in their proper relation. Since no further work is possible in the near future, the results are published in the hope that they may be of use elsewhere.

EXPERIMENTAL

Apparatus

All measurements of light absorption were carried out quantitatively by means of a Judd Lewis sector photometer (Hilger H-41) and Hilger E-2 spectrograph. The light source was an under-water tungsten spark (3). Spectra were photographed on Wratten and Wainwright panchromatic plates. Points of equal density on paired spectra were found by use of a Moll type A microphotometer especially adapted to the work by adding a longer galvanometer scale, a more powerful light source, and an elevating lever for rapid shift from one spectrum to the other. Match points were marked on the emulsion by a fine scratch and their wave lengths were later read off from calibrated wave length scales photographed on the plate.

Instead of diluting with a solvent to obtain high values of the extinction coefficient we had to use extremely thin layers of the melted compounds. Absorption cells as shown in figure 10 were therefore constructed. Fused quartz plates 2 x 2 cm. square x 3.5 mm. thick, ground optically flat to a tolerance of 0.001 mm. were spaced apart by thin strips of pure gold, 2 mm. wide by 2 cm. long, which were laid along two sides and the bottom. The thickness of the gold varied from 0.075 to 0.005 mm. depending on the range of log K required, the thinnest layer permitting a value for log K of 3.5 to be measured. All metal parts of the cell were heavily gold plated to resist corrosion by the quinones.

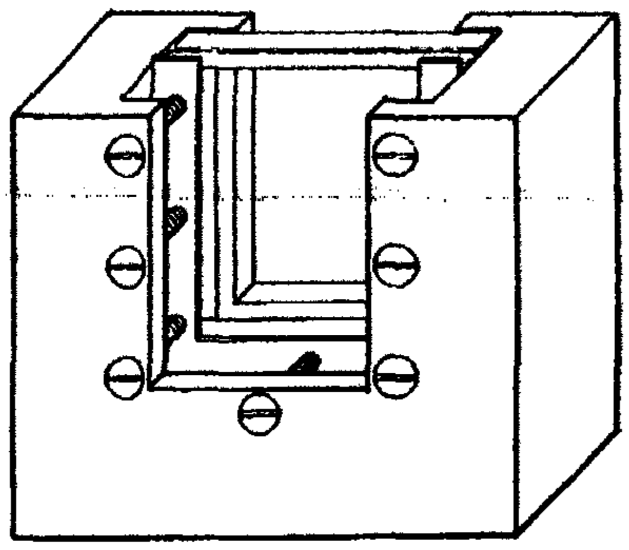

Fig. 10

As it was necessary to keep the mixture molten while spectra were being taken, a cell heater was constructed to set on the table of the photometer in place of the usual cell supports. This was of sheet iron construction inside and out, insulated electrically with mica and thermally with magnesia. Windows of 2-cm. brass tubing provided passage for the two light beams of the photometer. The two windows at the end nearest the spectrograph were closed on the inside with thin quartz discs to prevent vapors from condensing on the collimating lenses of the photometer. The other windows were left open to prevent the accumulation inside the heater of sufficient vapor to affect the results. Heat was applied electrically by resistance wire wound around the core and regulated with a lamp bank to give a temperature about two degrees above the melting point of the substances studied.

Technique

In the assembly of the absorption cells, the quartz plates were first cleaned with extreme care. All subsequent handling was done with smooth-jawed brass forceps. After assembly, the cell thickness was made uniform by adjusting the seven small screws bearing against the U-shaped strip of brass. The cell was viewed by reflected light from a Pyrex mercury arc, and adjustment was varied until the interference bands which appeared were lined vertically with the cell and as few in number as possible. A minute variation in thickness across the cell was of slight concern, since in measuring both cell thickness and light absorption an average value was obtained; variation from top to bottom caused a gradation in density across the spectrum, however, and was avoided.[4] The empty cell after adjusting as above, was held at the slit of a spectrograph and illuminated by a powerful continuous light source.[5] The spectrum of the empty cell was photographed and adjacent to it the mercury arc spectrum. The number of dark interference bands between two lines in the mercury arc was counted. The cell thickness was then found using the formula:

$$d = \frac{\frac{n}{2}}{\frac{1}{\lambda_1} - \frac{1}{\lambda_2}}$$

where d = thickness of cell, and

n = the number of dark bands between wave lengths λ_1 and λ_2.

Unless the cell was of uniform thickness from top to bottom, the interference bands were sloped and indistinct.

Two cells were placed in the heater. One contained the melted compound; the other, containing the "solvent," served to correct for light reflected from the faces of the first cell and for light absorbed by the "solvent." In taking the spectra of pure quinones this second cell was empty, the two quartz plates being spaced to avoid interference bands.

Equimolecular amounts of the quinone and "solvent" were weighed into a test tube made of an 18-cm. length of 8-mm. Pyrex tubing. A 20-cm. length of 3-mm. tubing drawn to a tip at one end made a sort of elongated medicine dropper for transferring the melted substance from test tube to absorption cell. The tip of the dropper was placed at the space between the quartz plates. Providing the cell had been properly cleaned,

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[4] We are indebted to Professor Valasek of the Physics Department for suggesting the method of measuring cell thickness.

[5] Hilger E. I. spectrograph and 500-watt projection bulb.

surface tension then filled the cell completely. The cell was always inspected to see that no air bubbles remained.

Preparation and purification of materials

Dimethylaniline. The commercial product was treated with acetic anhydride, carefully fractionated under vacuum, and finally purified by three crystallizations from its own mother liquor. n_D^{20} 1.5570; given in the literature, 1.55873.

Hydroquinone dimethyl ether. Kahlbaum's product was twice fractionated *in vacuo*. Melting point 56°C.; given in the literature, 56°C.

Resorcinol dimethyl ether. Resorcinol was methylated with dimethyl sulfate and the crude product purified by steam distillation, vacuum distillation, treatment with metallic sodium, and again vacuum distillation. Boiling point, 82.5–84°C. at 5 mm.; given in the literature, 216.5–217.7°C. at 760 mm.

Veratrole. Guaiacol was methylated with dimethyl sulfate and the product twice vacuum distilled. The fraction boiling at 100–106°C. at 18 mm. was partially frozen and the crystals separated. This was repeated six times, the melting point rising to 22°C.; given in the literature, 23°C.

Anisole. Anisole was purified by vacuum distillation. Boiling point, 65°C. at 20 mm. $n_D^{21.8}$ 1.5153; given in the literature, 1.51503.

p-Xylene. Kahlbaum's product was used without purification. Melting point, 12–14°C.; given in the literature, 16°C.

Mesitylene. Eastman's product was used without purification. $n_D^{14.6}$ 1.5000; given in the literature, 1.4966.

Dibenzyl. This was made according to the directions of Cannizzaro and Rossi (4). The crude product was recrystallized three times from alcohol using charcoal. It was then recrystallized twice from purified ether. Melting point, 51.5–52.5°C.; given in the literature, 52.5°C.

Tolane. Stilbene dibromide was treated under a reflux condenser for eight hours with a slight excess of saturated alcoholic potassium hydroxide. The potassium bromide was filtered off and the liquid returned to the flask with addition of a small amount of solid potassium hydroxide for another eight hours. The product was poured into ice water; the oily layer was separated, dried, and distilled *in vacuo*. The tolane fraction was recrystallized from alcohol four times, twice vacuum distilled, and again crystallized from absolute alcohol. Melting point, 60°C.; given in the literature, 60°C.

Chloroquinone. A mixture of 30 g. of chlorohydroquinone, 300 cc. of purified ether, and 200 g. of finely divided lead dioxide was stirred for 10 minutes, after which the lead dioxide was filtered off and washed well with ether. The combined ethereal solutions were evaporated to a volume of

200 cc. and crude chloroquinone crystallized out by freezing in a carbon dioxide–ether bath. Repeated recrystallizations from absolute ether gave a product melting at 57°C. (literature, 57°C.).

Quinone. Crude quinone was purified by several sublimations. Melting point, 113.5–114.5°C.; given in the literature, 115.7°C.

Toluquinone. This was prepared from *o*-toluidine by Nietzki's method (5). It was purified by repeated recrystallization and sublimation. Melting point, 67–67.5°C.; given in the literature, 69°C.

p-Xyloquinone. *p*-Xylidine was oxidized by Nietzki's method (5). It was purified by repeated recrystallization and sublimation. Melting point, 123–124°C.; given in the literature, 125°C.

Durene and duroquinone. These substances were obtained in a pure state from Professor L. I. Smith, to whom we are very deeply grateful. The melting points and boiling points given are uncorrected. Refractive indexes were determined with an Abbé refractometer. All quinones were repurified just preceding use.

SUMMARY

1. The absorption spectra of chloroquinone, benzoquinone, toluquinone, xyloquinone, and duroquinone were measured quantitatively in the absence of solvent.

2. A technique is described for obtaining quantitative light absorption measurements on thin layers of liquids or melted solids.

3. The absorptions of equimolecular mixtures of the above quinones with aromatic hydrocarbons, ethers, and amines were measured. A variation in the effect of these "solvents" on the spectra of the quinones was observed, ranging from very pronounced color changes attributed to molecular compound formation to slight changes of the order of "solvent effects."

4. The changes from the absorption spectra of quinones in a pure state to the spectra in molecular compound forming "solvents" have been correlated with the known oxidation-reduction potentials of the quinones.

5. Two generalizations have been found:

I. In a series of quinones the change in the absorption spectrum brought about by a "solvent" capable of forming molecular compounds, increases with increasing oxidation-reduction potential of the quinones.

II. The order in which "solvents" fall with respect to increasing effect on the absorption spectrum of a quinone is independent of the quinone studied.

We wish to express our thanks to both the Physics Department and the Biophysics Department of the University of Minnesota for their valuable aid in supplying equipment and suggestions as to its use.

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CHEMICAL ACTION IN THE GLOW DISCHARGE. XI

The Decomposition of Nitrogen Dioxide and the Nitrogen Dioxide Equilibrium

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INTRODUCTION

The present study of the decomposition of nitrogen dioxide in the glow discharge was undertaken for the purpose of determining the limiting yields as well as the principles underlying the fixation of nitrogen in the electric arc. Attention was also given to the mechanism of reaction involved.

APPARATUS AND METHOD

The apparatus and method of procedure were essentially the same as those used for the decomposition of nitrous oxide (1). A discharge tube of the type illustrated in figure 4 was enclosed in an electric furnace and the temperature maintained constant at 170°C., except in the experiment on the temperature coefficient. This temperature was chosen so that the gas would be entirely in the form of NO_2. Pressure changes were read with a Nujol oil manometer; the system was kept free of mercury vapor. The nitrogen dioxide was obtained from a reservoir of liquid nitrogen dioxide made by the arc process.

RESULTS

The discharge current

The relative rates of decomposition of nitrogen dioxide in the negative glow and positive column, as determined by the discharge current, are shown in figure 1. Line 1 is for the negative glow and line 2 for the negative glow and positive column combined. The difference between lines 1 and 2 gives the relative rate for the positive column alone, while the difference between lines 1V and 2V gives the potential drop in this region.

It will be observed that the rates are proportional to the current in both the negative glow and positive column. The yield measured from the slopes of the lines is 21 molecules decomposed per electron of current in the negative glow, 80 molecules per electron in the positive column and negative glow combined, and 59 in the positive column alone. The proportionality between current and rate shows this reaction to behave similarly to the other reactions described in this series.

The voltage curves 1V and 2V give an indication of the power consumed per molecule for various discharge currents. The conspicuous difference in the two regions of the discharge is that the rate is proportional to the power input in the negative glow, while in the positive column the voltage, and hence the power consumed, drops naturally as the current increases.

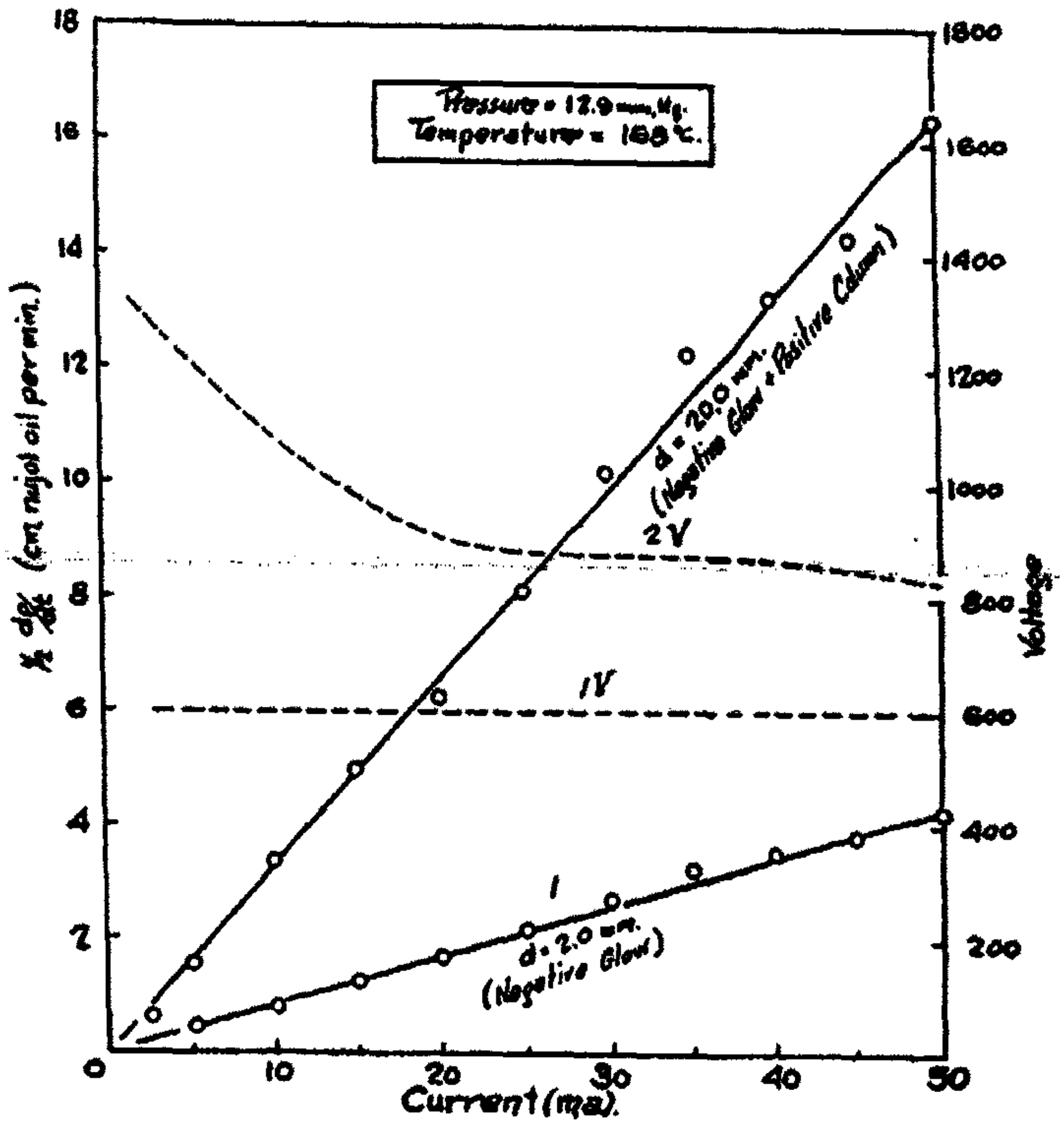

FIG. 1. RELATIVE RATES OF DECOMPOSITION OF NITROGEN DIOXIDE IN THE NEGATIVE GLOW AND POSITIVE COLUMN

The pressure

This reaction is again similar to the others studied in this series in that the rate of reaction in the negative glow is independent of the initial pressure of nitrogen dioxide between wide limits. The electrochemical equivalence law,

$$\frac{dP}{dt} = \alpha I$$

enunciated for the discharge is still applicable.

The effect of pressure in the positive column is difficult to determine since the power input and effective length of the column both vary with the pressure.

The power efficiency

The power consumed per molecule decomposed in the various regions of the discharge is illustrated in figure 2.

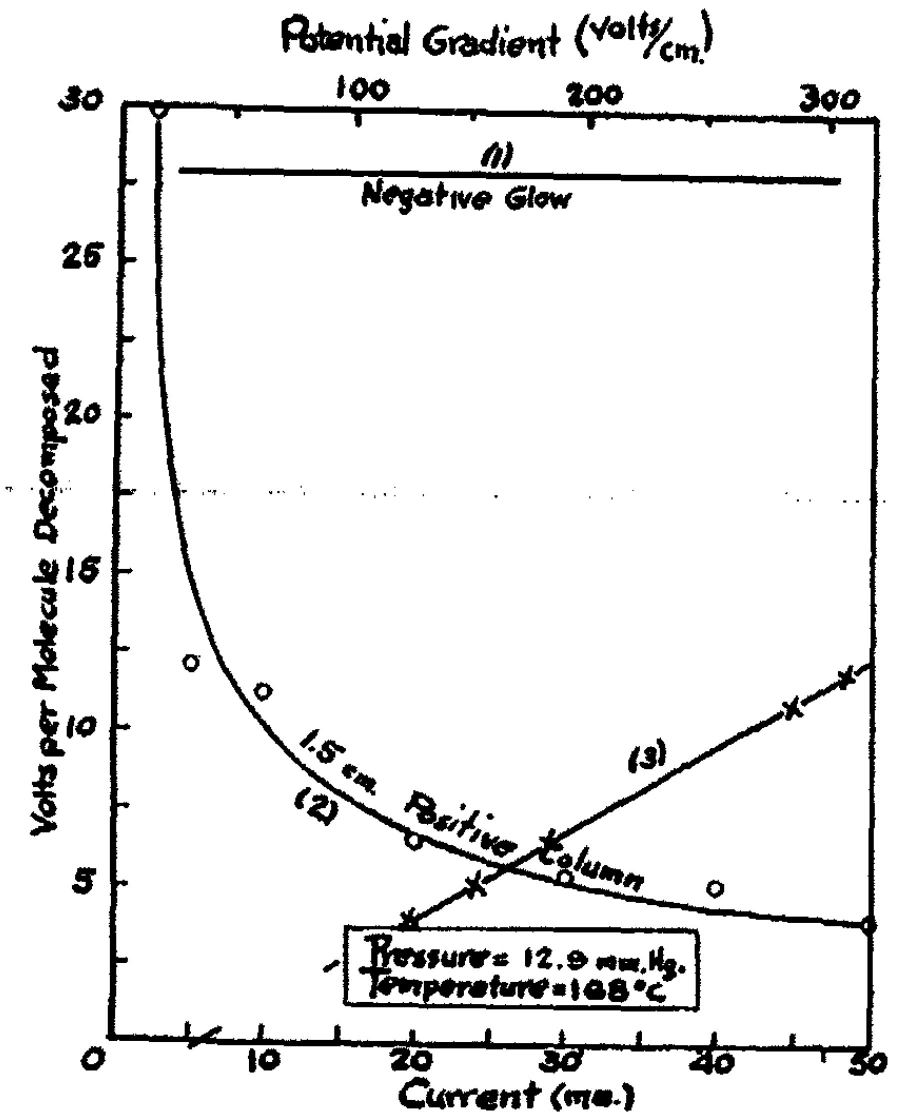

FIG. 2. POWER CONSUMED PER MOLECULE DECOMPOSED IN THE VARIOUS REGIONS OF THE DISCHARGE

Line 1 shows the power consumption to be constant in the negative glow from 2.5 to 50 ma., and is equivalent to approximately 28 electron volts per molecule (V_e/M) decomposed.

The results obtained in the positive column are shown by line 2. It will be noted that the efficiency changes from $V_e/M = 30$ at 2.5 ma. current to $V_e/M = 4$ at 50 ma. This increase in efficiency is due entirely to a decrease in potential gradient, since line 2 of figure 1 shows the rate to be proportional to the current.

The change in efficiency with respect to potential gradient is shown by line 3, in which it will be seen that V_e/M decreases linearly with the potential gradient throughout the column; the gradients given are those obtained with the various discharge currents.

Foreign gases

The effect of foreign gases on the rate of decomposition is illustrated in figure 3.

Especial attention is called to the fact that nitrogen and oxygen are very similar in their effects on the rate of decomposition, oxygen if anything being slightly more efficient. The rate of decomposition is slowed down even less by helium than by oxygen.

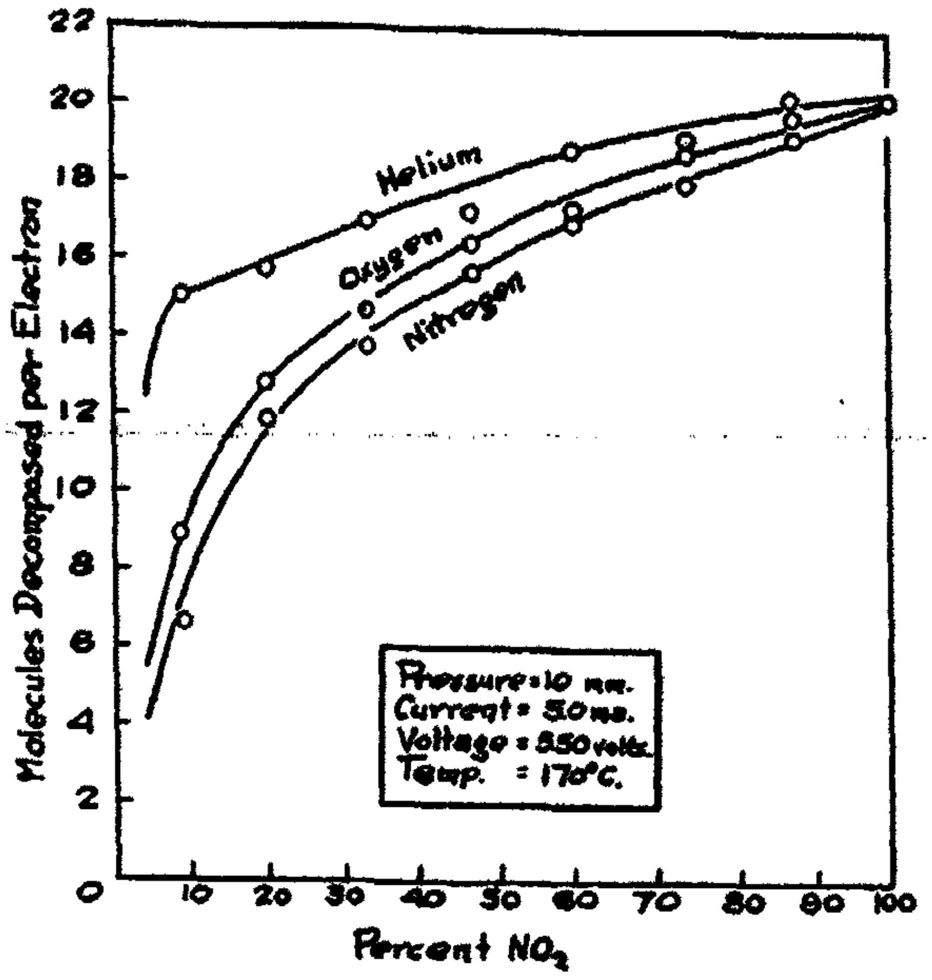

FIG 3. THE EFFECT OF FOREIGN GASES ON THE RATE OF DECOMPOSITION OF NITROGEN DIOXIDE

The above results are in distinct contrast to those obtained with nitrous oxide wherein the retardations in rate of dissociation in the presence of nitrogen, oxygen, and helium were proportional to the partial pressure of nitrous oxide times the relative probabilities of ionization (Θ) of their gases. In the case of nitrous oxide, therefore, these foreign gases contributed nothing to the rate of decomposition. To say in the present case that activated nitrogen, for instance, did not decompose nitrogen dioxide it would be necessary to assign values of $\Theta = 1$ to helium, $\Theta = 3$ to nitrogen, and $\Theta = 31$ to nitrogen dioxide, i.e., the probability for ionization in nitrogen dioxide must be over ten times that in nitrogen. Lind (2) assigns values to the stopping powers of these gases for α rays of 111 for nitrogen dioxide and 99 for nitrogen; thus the ionization efficiency in the two gases is nearly the same. It must be concluded, therefore, that an activated helium, oxygen, or nitrogen molecule is almost as effective in inducing decomposition as is an activated nitrogen dioxide molecule itself.

Temperature

The effect of temperature on the rate of dissociation is shown in figure 4. The runs were carried out at constant gas density from room temperature to 225°C. The voltage remained fairly constant over the entire temperature range.

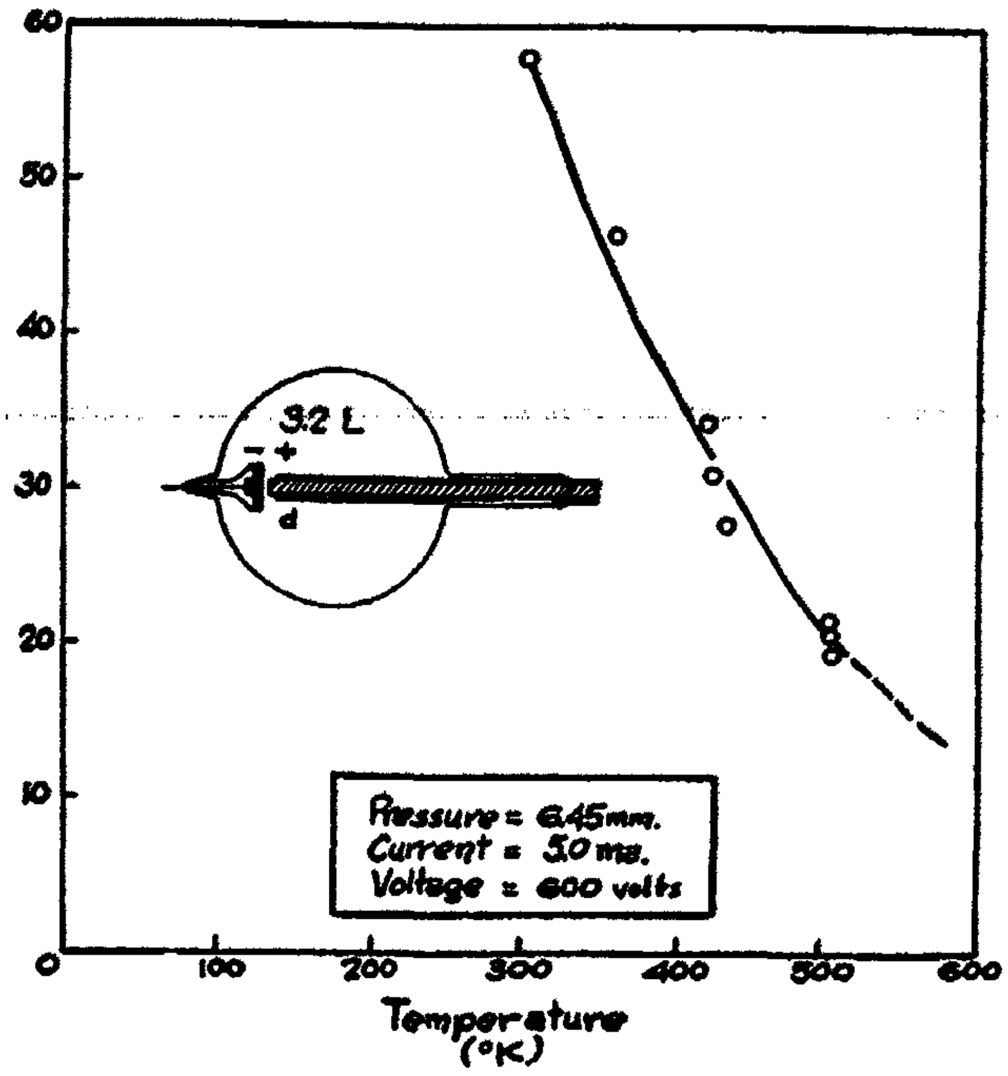

Fig. 4. The Effect of Temperature on the Rate of Decomposition of Nitrogen Dioxide

The conspicuous and surprising thing to note in these experiments is that the number of molecules decomposed per electron decreased almost linearly with temperature over the range investigated. At 225°C. about 30 electron volts are required to decompose one molecule, while at room temperature this value drops to 10 electron volts.

Equilibrium

The $2NO_2 \rightleftharpoons N_2 + 2O_2$ equilibrium was measured by running the discharge in a $N_2/2O_2$ mixture for about an hour at room temperature until equilibrium was established. The pressures ranged from 5 to 10 mm. of mercury. Liquid air was then applied to the discharge tube and the nitrogen dioxide frozen out. The nitrogen and oxygen were next pumped off, the nitrogen dioxide was allowed to evaporate, and the pressure measured with an oil manometer. The results showed the nitrogen dioxide pressure to be 1.6 per cent of the initial pressure.

The rate of synthesis of nitrogen dioxide in a liquid air-cooled tube of the type used in the decomposition experiments yielded 1.58 molecules of nitrogen dioxide per electron of current. Referring to figure 3 it will be seen that the rate of decomposition of nitrogen dioxide in a mixture containing approximately 1.5 per cent nitrogen dioxide and 98.5 per cent nitrogen or oxygen is equal to the observed rate of synthesis in a $N_2/2O_2$ mixture. The equilibrium value of 1.6 per cent nitrogen dioxide is, therefore, substantially correct.

DISCUSSION OF RESULTS

The general interpretation to be given to these results is necessarily the same as that applied to the other reactions studied in this series, namely, that the reaction is brought about by positive ions formed in the discharge. The first step in the decomposition process is the formation of an NO_2^+, and N_2^+ or an O_2^+ ion. The second step consists of the dissociation of nitrogen dioxide by the ion so formed.

A calculation of the number of molecules decomposed per ion in the negative glow can be made from an evaluation of the number of ions formed for each electron leaving the cathode. Since the positive ion current to the cathode is negligible (3), and since the electrons leaving the cathode receive an energy corresponding to the cathode potential drop, the number of positive ions formed per electron of current may be estimated directly from the results of Lehman (4) and of Anslow (5). Lehman obtained 13 ions per 600 volt electron, i.e., an expenditure of 45 volts per ion in nitrogen. Anslow, using a similar method, obtained a somewhat lower value of 5.9 ions for a 600 volt electron. Langmuir and Jones (6) obtained a value of about 85 volts per ion, which is equivalent to 7 ions per 600 volt electron.

Figure 3 shows 20 molecules of nitrogen dioxide to be decomposed per electron. According to Lehman's value, therefore, the number of molecules decomposed per NO_2^+ ion is $M/N = 20/13 = 1.55$. Anslow's value gives $M/N = 20/5.9 = 3.4$, while from Langmuir and Jones the ratio $M/N = 20/7 = 2.8$ is obtained. It will be seen from this that an estimation of the M/N ratio necessarily involves an uncertainty factor of 2. Since the results of Lehman appear the most consistent, it is probable that the correct value at 170°C. is $M/N = 1.55$ or possibly 2. At room temperature, however, the M/N ratio is approximately three times that for 170°C.

An estimation of the M/N ratio in the positive column is speculative, since there exists no reliable method for computing the number of ions formed per electron of current. Assuming the same voltage efficiency in the positive column as in the negative glow a ratio of $M/N = 10$ is obtained at 50 ma. current. This value is necessarily high but serves as an upper limit. At 2.5 ma. the ratio falls to $M/N = 1.5$. It is reasonable to assume, therefore, that the true M/N ratio is essentially the same in the two regions of the discharge.

The results presented in the series of studies on the synthesis and decomposition of nitrogen dioxide in the discharge show directly the limits that may be obtained in the arc process for the fixation of nitrogen. In the synthesis (7) it has been shown that it is possible to remove the nitrogen dioxide from the arc as fast as formed by cooling the discharge tube with liquid air. In this case the reaction $N_2 + 2O_2 = 2NO_2$ goes to completion. The great source of energy loss results from the fact that only N_2^+ ions contribute to the formation. On the other hand it is to be seen from the present paper that N_2^+, O_2^+, and NO_2^+ ions all contribute to dissociation, hence the rate of dissociation is rapid compared to synthesis. For this reason the equilibrium value is low, being of the order of 1.6 per cent nitrogen dioxide. Thus the lower limit for the above equation is 1.6 per cent on the side of nitrogen dioxide where the rates of synthesis and decomposition are equal, and 100 per cent when decomposition is eliminated. In practice, therefore, the yield must depend on the rapidity with which nitrogen dioxide is removed from the discharge. It is interesting to note that the equilibrium will be practically the same in air as in an $N_2/2O_2$ mixture, since both the rates of synthesis and decomposition are the same under these conditions.

MECHANISM OF REACTION

There are two probable mechanisms for the reaction about the ion when once formed. One is the step or quasi molecule mechanism, generally considered in photochemical reactions. It involves dissociation according to the equation:

$$NO_2 \rightarrow NO + O$$

This step is impossible in the present case since it would necessitate a retardation in rate by oxygen; the possibility of nitric oxide being decomposed before being carried out of the discharge by convection is small. Figure 3 shows the dissociation in oxygen to be slightly greater than in nitrogen. Again such a mechanism would demand a positive and not a negative temperature coefficient since the rate of oxidation of nitric oxide increases with decreasing temperature. It must be concluded, therefore, that the production of nitric oxide is not a step in the reaction mechanism.

The second possible mechanism for decomposition is one involving ion clusters. An ion cluster of the form ($NO_2^+ NO_2$) or ($N_2^+ \cdot 2NO_2$) is considered as decomposing directly into $N_2 + 2O_2$. This mechanism is in accord with the observed negative temperature coefficient since the dielectric constant, and hence the clustering ability of nitrogen dioxide, increases with decreasing temperature. It is interesting to note that the presence of such clusters has been shown to exist in mixtures of nitrogen and oxygen by mass spectrograph measurements by Luhr (8). The cluster mechanism will be discussed in more detail in a later communication.

SUMMARY

The decomposition of nitrogen dioxide in the glow discharge is shown to obey the same electrochemical equivalence law given for the other reactions studied in this series.

The decomposition is shown to be brought about with almost equal ease by NO_2^+, N_2^+, O_2^+, and He^+ ions.

The M/N ratio at 170°C. is calculated for the negative glow and positive column. The ratio lies between $M/N = 1.55$ and $M/N = 3$. The lower value is the more probable.

The decomposition has a strong negative temperature coefficient, the M/N ratio being three times as large at room temperature as at 225°C.

A value of 1.6 per cent is obtained for the amount of nitrogen dioxide in the arc at room temperature under equilibrium conditions. This is discussed in connection with the possible yields that can be obtained in the arc process for nitrogen fixation.

The results are interpreted as indicating that the decomposition cannot be by step mechanism involving the formation of nitric oxide. It is suggested that the cluster type mechanism will best account for both the rate decomposition and the negative temperature coefficient.

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CHEMICAL ACTION IN THE GLOW DISCHARGE. XII

THE DISSOCIATION OF AMMONIA[1]

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The catalytic, alpha ray, and photochemical decomposition of ammonia have been so extensively discussed in the recent literature that it has seemed advisable to contrast these results with those obtained in the glow discharge.

APPARATUS AND METHOD

In general the method of procedure in this work is similar to that used for the decomposition of nitrous oxide (1). The types of discharge tubes used are illustrated in the inset to figure 1 of this paper and figure 1A of the nitrous oxide paper. The temperature coefficient was obtained by enclosing the entire tube (figure 1A) in an electric oven. The pressure changes were read with a McLeod gauge, or with a Nujol oil differential manometer. The gases used were purified and stored as described in previous articles of this series.

The rate of reaction was determined from the initial slope of the line in time vs. pressure curves. Since the curves were usually straight lines over the first half of the pressure rise little difficulty was experienced in obtaining accurate initial rates.

RESULTS

The effect of ammonia pressure

The rate of decomposition at various initial pressures of ammonia is given in table 1.

It will be noted that the rate of reaction, R, as well as the efficiency, M/V, remain constant from below 4 mm. to about 16 mm. The efficiency varies little at lower pressures, although the rate and voltage both increase. At pressures above 16 mm. the appearance of the discharge changes entirely. The general glow disappears and thread-like arcs appear between the electrode; under these conditions the efficiency at least doubles.

The independency of the rate on the ammonia pressure between wide limits shows this reaction to be similar to others studied in this series. The

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[1] This work was carried out under the direction of Dr. A. Keith Brewer.

enhancement of the rate accompanying the change in appearance of the discharge and drop in the cathode potential above 16 mm. is unique to ammonia decomposition. This peculiar behavior in ammonia is doubtless occasioned by its remarkable ability to lower the cathode potential drop by changing the "work function" of the surface.

The fact that the rate is independent of the pressure has an analogue in the photochemical decomposition, where Wiig and Kistiakowsky (2) have shown the quantum yield to be independent of the pressure from 800 to 1 mm.

TABLE 1

Rate of decomposition at various initial pressures of ammonia

PRESSURE OF AMMONIA	RATE	V (cathode fall)	M/e (molecules per electron)	V/M (electron volts per molecule)
mm. Hg	*mm. per minute*			
0.5	0.284	718	4.72	152
4.0	0.138	331	2.34	141
16.0	0.138	339	2.34	145
32.0	0.220	253	3.74	67.6

The discharge current

The effect of current on the rate of decomposition in the negative glow and in the negative glow and positive column combined is shown in figure 1. It will be noted that the rate is proportional to the current in both regions of the discharge. This, combined with the independence of rate on pressure, enables the decomposition to be expressed by the simple equation $dP/dt = \alpha I$, as in the case of all other reactions studied in the glow discharge. A linear current relationship was also obtained by Davies (3), using Siemens' type of discharge.

The significant point to note in these results is that the proportionality between current and rate is a direct indication that the decomposition is a primary process; the initiation of the reaction, therefore, results from a direct collision between an electron and an ammonia molecule, or some other molecule capable of inducing decomposition. The initial and rate-determining steps cannot, therefore, involve any interaction between activated states.

Added gases

The rates of dissociation of ammonia in the negative glow in the presence of various gases are given in table 2.

The values for the electron volts required to dissociate one molecule (V/M) show only a small gradual increase up to 80 per cent added gas in

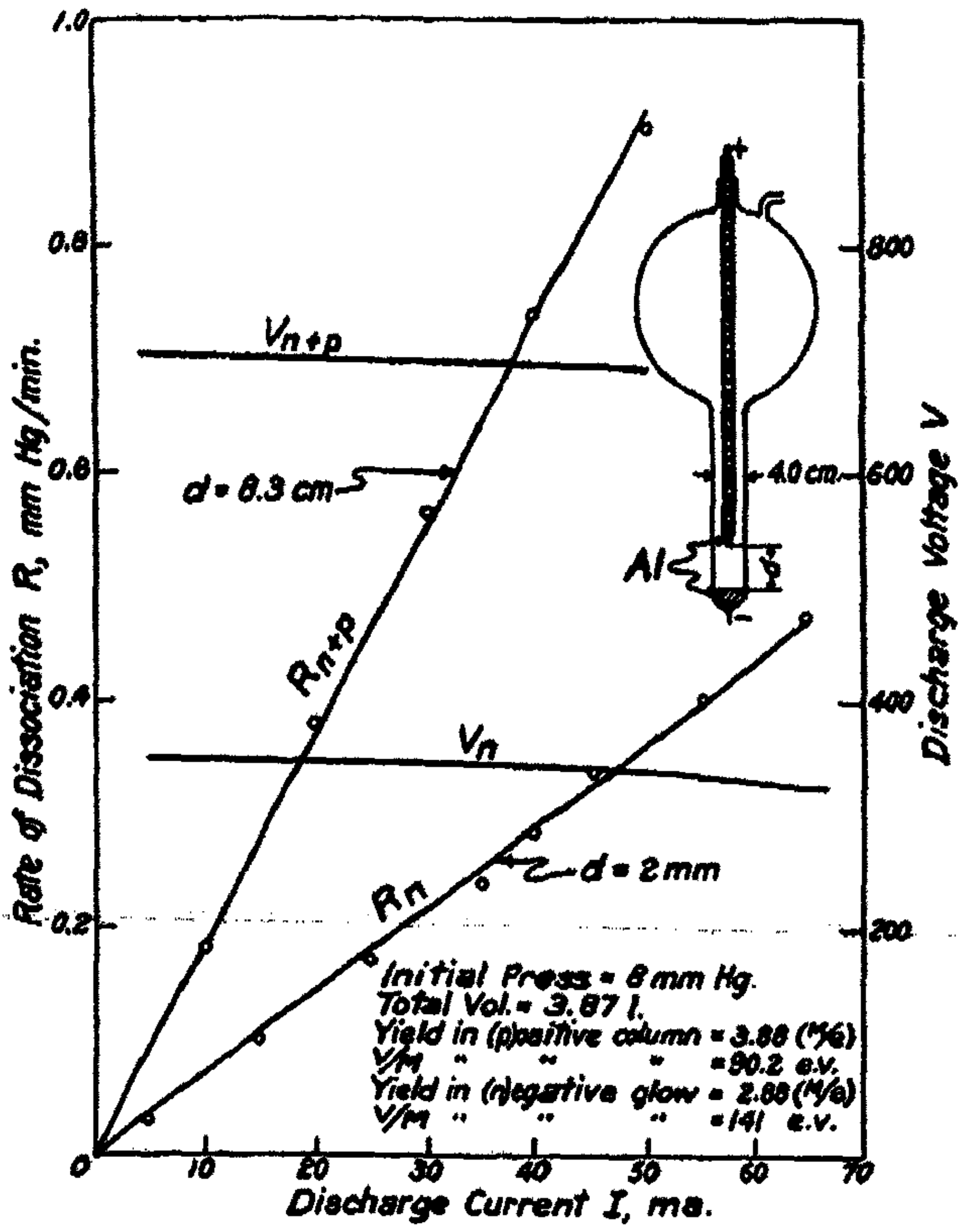


FIG. 1. EFFECT OF CURRENT ON THE RATE OF DECOMPOSITION

R_n and V_n give rate and voltage in negative glow; electrode separation 2 mm. R_{n+p} and V_{n+p} give rate and voltage in combined negative glow and positive column; electrode separation 8.2 cm.

TABLE 2

Rates of dissociation of ammonia in the negative glow in the presence of various gases

ADDED GAS	RATE	V (cathode fall)	M/V	V/M (electron volts per molecule)
	mm. per minute			
None	0.214	390	3.42	114
80 per cent nitrogen	0.174	400	2.78	144
80 per cent hydrogen	0.086	430	1.38	312
80 per cent (N_2 + $3H_2$)	0.162	385	2.59	155
80 per cent helium	0.174	420	2.78	151
80 per cent argon	0.176	315	2.82	112
50 per cent oxygen	0.221	415	3.32	125

every case except for hydrogen. Above 80 per cent the rate in all cases drops rapidly to zero at 100 per cent added gas. It follows, therefore, that ions of these various gases are about as efficient catalysts for the decomposition of ammonia as are NH_3^+ ions themselves. In the case of hydrogen, however, the rate decreases for various partial pressures of added hydrogen in proportion to the number of H_2^+ ions present. Indeed, the computed curve for the number of NH_3^+ ions formed as given by the relative ionizing efficiency of an electron in ammonia and hydrogen mixtures follows the rate curve almost exactly in a manner analogous to that shown in figure 7 of paper XI of this series (4). It must be concluded, therefore, that H_2^+ ions do not catalyze the decomposition. The retarding effect of hydrogen cannot be due to the interaction of hydrogen atoms, and NH or NH_2 as is postulated in the photochemical decomposition by Melville (5) since the absence of N_2H_4 in the negative glow, as later described, suggests the absence of NH and NH_2. Again this mechanism demands that $H + NH_2 \rightarrow NH_3$ increase with the square of the current if the production of H and NH_2 are each proportional to the current; the observed dissociation, however, is proportional to the current. It should be added that convection was sufficiently rapid so that the chance of a quasi molecule such as NH_2 being struck by an electron before being carried out of the path of the discharge was negligible.

TABLE 3

The effect of Hg^+ ions on the decomposition of ammonia

TEMPERATURE	PRESSURE	PER CENT Hg	RATE	M/e (molecules per electron)	V/M (electron volts per molecule)
degrees C.	*mm.*		*mm. per minute*		
25	5.95	0	0.236	3.54	110
163	9.55	19	0.211	2.45	153
191	12.9	37	0.276	3.05	130

Oxygen up to a partial pressure of 75 per cent behaves in a manner identical to that of nitrogen or argon. Above this pressure the rate falls rapidly to zero. Since the oxidation of ammonia to nitrogen dioxide and water would show a decrease in pressure, and since the oxidation of the hydrogen alone would show only a slight increase, it seems likely, in view of the large pressure increase observed, that O_2^+ ions dissociate ammonia in a manner similar to N_2^+ and A^+ ions, and that no appreciable oxidation of the ammonia occurs under 75 per cent oxygen. In this respect oxygen in the negative glow behaves less effectively than in the photochemical decomposition described by Taylor and Salley (6) in which they found the rate to be increased some fourfold by oxygen. The fact that O_2^+ ions do not react with the hydrogen to form water is not surprising, as it has been shown that this reaction is initiated entirely by H_2^+ ions, the O_2^+ ions being inert (7). Since only initial rates were used, the production of H_2^+ ions was negligible.

In determining the effect of Hg^+ ions it was necessary to vary the temperature to give different mercury pressures. The results obtained are given in table 3.

Since these data could not be obtained under constant conditions, some scattering in the value of V/M is to be expected. The results indicate, however, that Hg^+ ions behave similarly to N_2^+ ions in catalyzing decomposition. The ionization potential of mercury being considerably lower than that of ammonia suggests that it is not necessary for the charge to be transferred to the ammonia molecule for decomposition to occur about the ion.

Equilibrium

The ammonia synthesized at room temperature in a discharge, run in an $N_2/3H_2$ mixture until equilibrium was established, was frozen out with liquid air, and the nitrogen and hydrogen were pumped off. The ammonia was then allowed to evaporate and the pressure was read. The ammonia so formed represented an average of 5.55 per cent of the initial amount by volume. The amount of ammonia remaining from a similar test, starting with pure ammonia, was 6.56 per cent. Thus the most probable value for the equilibrium at room temperature in the negative glow is about 6 per cent.

This equilibrium value is in agreement with 6 per cent reported by Davies (3) for the Siemens' tube, but is somewhat higher than the alpha ray value, 4.7 per cent, obtained by d' Olieslager and Jungers (8).

Reaction products

The total pressure increase invariably showed the final decomposition to go almost completely to nitrogen and hydrogen. Attempts were made to detect hydrazine by immersing the discharge in dry ice and alcohol. No hydrazine was frozen out in the negative glow; in the positive column, however, at 1 mm. pressure and 20 ma. current, a condensible product was obtained equivalent to one molecule for every ten ammonia molecules decomposed. At 8 mm. pressure no condensible product could be detected, nor could any be detected at any pressure when dry ice was applied to the discharge tube after the ammonia had been 50 per cent or more decomposed.

These results indicate that the decomposition ordinarily goes to instantaneous completion in the discharge. In this respect they differ from the findings of Bredig, Koenig, and Wagner (9), who obtained as high as 80 per cent conversion to hydrazine at low pressures and high current densities when ammonia was drawn through the discharge. Gedye and Allibone (10) obtained appreciable quantities of hydrazine with cathode rays at low pressures. The results are in agreement in that in all cases low pressures favored the production of hydrazine.

The temperature coefficient

The influence of temperature on the number of molecules dissociated per electron (M/e) is shown by curves 1, 2, and 3 of figure 2. Each curve was taken at constant gas density; the voltage did not change with temperature.

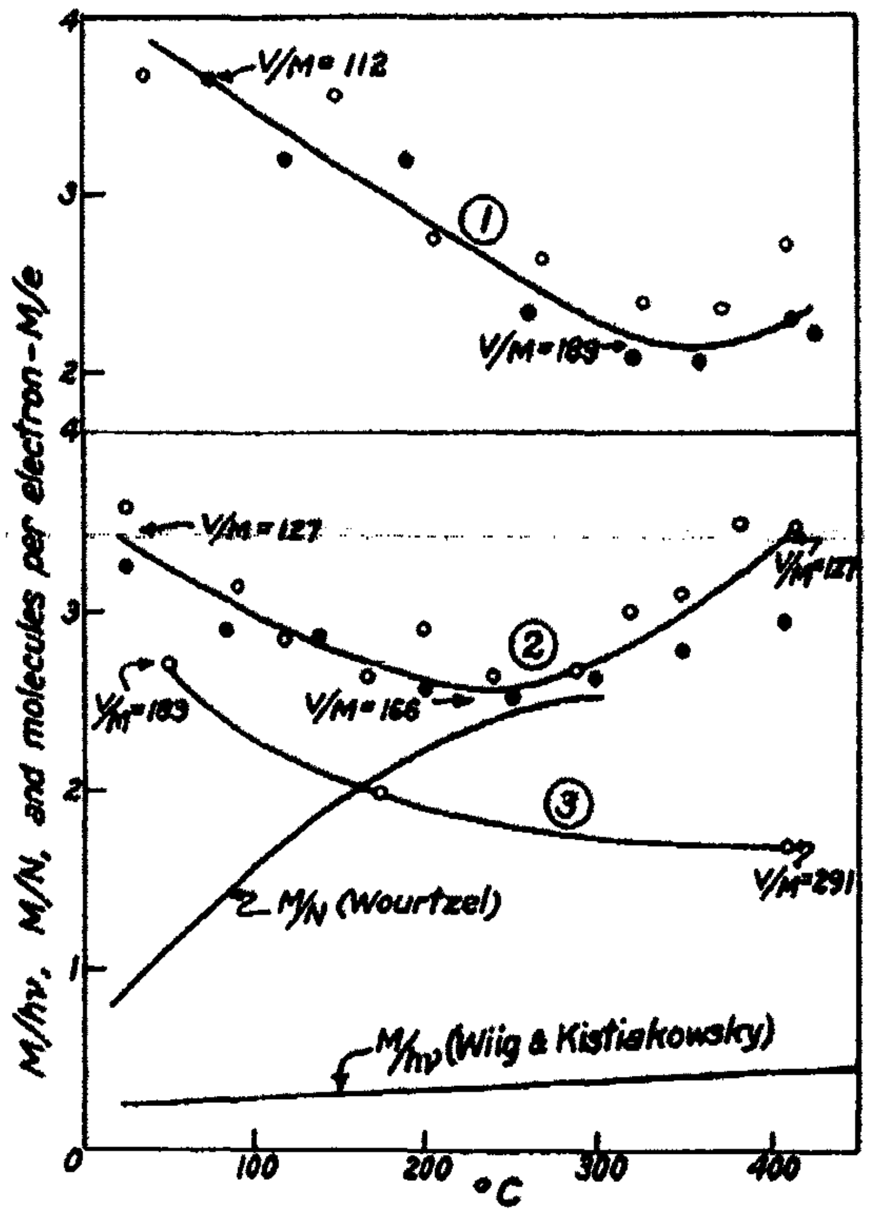


FIG. 2. EFFECT OF TEMPERATURE ON THE RATE OF DISSOCIATION
Curve 1: P = 1.3 mm. at 25°C., I = 5 ma., V = 415 volts.
Curve 2: P = 5.5 mm. at 25°C., I = 20 ma., V = 431 volts.
Curve 3: P = 5.5 mm. $NH_3 - H_2$ mixture at 25°C., I = 20 ma., V = 495 volts.

The curves show a temperature coefficient of less than unity, i.e., about 0.983 per 10°C. The coefficient becomes unity for curves 1 and 2 at 350°C. and 250°C., respectively, and shows a positive value at still higher temperatures; curve 3, with 50 per cent hydrogen, is less than unity throughout the entire temperature range.

The results of Wourtzel (11) for alpha rays and those of Wiig and Kistiakowsky (2) for photochemical dissociation are also shown for comparison.

Kuhn (12) obtained a temperature coefficient for photochemical decomposition comparable to that given by Wourtzel, but observed a retarding effect in hydrogen similar to curve 3.

The fact that curve 1 shows a more pronounced decrease in rate than does curve 2, indicates that the decrease in rate with temperature is encouraged by low pressures. Probably it is for this reason that the present results differ from those of Wourtzel.

The cathode surface

The results which have been discussed so far have been for a "worked in" cathode. This particular reaction shows a far greater cathode aging effect than that usually encountered in the discharge (13). For instance, a freshly machined aluminum cathode gave a rate of 0.203 mm. per minute with a potential drop between the electrodes of 292 volts. This is equivalent to 84 electron volts per molecule dissociated. As the cathode aged the voltage increased while the rate decreased for a period of about three hours, after which the conditions remained fairly constant. The values for a worked-in cathode are given in figure 2; it will be noted that at room temperature from 112 to 127 electron volts are required per molecule.

An interesting side light to the above aging effect is that running the discharge in pure oxygen or hydrogen has no effect on the worked-in conditions, although a discharge in water vapor readily restores the original freshly machined characteristics. This is doubtless due to the reduction of a nitride film on the cathode, the formation of which is responsible for the aging effect.

The high rate of dissociation observed with freshly machined cathodes is intimately connected with the adsorption of ammonia on the surface, since under the conditions for high rate an abnormally low cathode potential drop was observed. The cathode potential drop is determined directly by the "work function" of the surface, being in general about one hundred times the work function. Brewer (14) has shown that the work function of a surface may be lowered from a third to a half by the adsorption of ammonia; this has been accounted for by the dissociation of the ammonia into ions by the surface forces. Since the lowering of the work function increases the ease with which electrons are emitted from the cathode, it should enhance the efficiency of the discharge.

A further possibility of accounting for the abnormally high rates on fresh surfaces may be had in the observation of Brewer that the ammonia adsorbed on metallic surfaces can undergo decomposition at a temperature as low as 250°C. While the surface was cold in the present case, it is probable that the bombardment by positive ions, atoms, and metastable molecules received by the cathode during the discharge would be as efficient as a hot surface in dissociating the adsorbed ammonia.

DISCUSSION OF RESULTS

The results just presented are similar to those previously obtained in the discharge, in that the rate is proportional to the current and independent of the pressure between wide limits. They possess two distinct differences, however, from those observed in the decomposition of nitrous oxide. The first is the pronounced cathode "working-in" effect already discussed. The second is in the effect of foreign gas ions. In the case of nitrous oxide the rate was determined solely by the rate of production of N_2O^+ ions; all other ions were without effect. In the present case, however, decomposition occurs almost as readily around N_2^+, O_2^+, He^+, A^+, and Hg^+ ions as about NH_3^+ ions; only H_2^+ ions are inert.

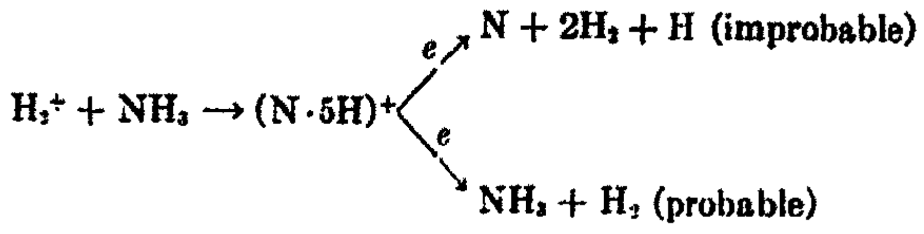
It is interesting to note that decomposition occurs about Hg^+ ions although the ionization potential of mercury is some 3 volts below that of ammonia. Thus it follows that a transfer of charge from the foreign ion to ammonia is unnecessary.

A determination of the number of molecules decomposed per ion (M/N) involves an uncertainty factor of 2, since various observers are in disagreement to this amount regarding the number of ions formed by an electron having an energy equal to the cathode fall of potential. Lehmann (15) gives 8 as the number of positive ions formed by a 350 volt electron. Anslow (16) obtained but 3.5 ions per 350 volt electron. The number of molecules decomposed per electron at 1.3 mm. is 3.7; the ratio, therefore, is $M/N = 3.7/8 = 0.46$, using the value of Lehmann, and $M/N = 3.7/3.5 = 1.1$ from Anslow's value. At somewhat higher pressures and especially at higher temperature the M/N ratio decreases from the values just given. Lind (17) gives $M/N = 0.8$ at room temperature. The best that can be said, therefore, is that the ratio is low, lying between 0.5 and 1.0.

MECHANISM OF DECOMPOSITION

The fact that the M/N ratio is less than 1.0 indicates either that all of the NH_3^+ ions do not undergo decomposition, or that there is an appreciable synthesis. The latter possibility is obviously impossible for initial rates and is not appreciable most of the time of a run, as can be seen from the equilibrium results. On the other hand, the inability of ions to cause dissociation can be accounted for on the basis of a cluster type of reaction mechanism.

An ion cluster upon disintegration may dissociate according to probability into its original constituents or into some new form. The data show that ammonia is not appreciably decomposed by H_2^+ ions; the formation and dissociation of the cluster, therefore, can be expressed by the process:



$$H_2^+ + NH_3 \rightarrow (N\cdot 5H)^+ \begin{array}{l} \overset{e}{\nearrow} N + 2H_2 + H \text{ (improbable)} \\ \underset{e}{\searrow} NH_3 + H_2 \text{ (probable)} \end{array}$$

In the cluster N is surrounded by 5 H; hence the chance for return to ammonia is high.

The conditions about N_2^+, He^+, A^+, O_2^+, and NH_3^+ ions are materially different. Thus

$$N_2^+ + NH_3 \rightarrow (3N\cdot 3H)^+ \begin{cases} \xrightarrow{e} N_2 + N + H_2 + H \text{ (probable)} \\ \xrightarrow{e} NH_3 + N_2 \text{ (small probability)} \end{cases}$$

and

$$NH_3^+ + NH_3 \rightarrow (2N\cdot 6H)^+ \begin{cases} \xrightarrow{e} N_2 + 3H_2 \text{ (probable)} \\ \xrightarrow{e} 2NH_3 \text{ (probable)} \end{cases}$$

In these two cases the N is not completely surrounded by H; the possibility of ammonia splitting out of the cluster, therefore, is much smaller than for the H_2^+ ion clusters.

SUMMARY

1. Ammonia is shown to decompose into the elements in the glow discharge. Some hydrazine is formed in the positive column but none in the negative glow.
2. The rate of decomposition is proportional to the current and independent of the pressure.
3. The ability of ammonia to dissociate into ions on the cathode surface results in abnormal reaction rates at higher pressures and for freshly machined surfaces.
4. The equilibrium between NH_3 and $N_2/3H_2$ is approximately 6 per cent NH_3.
5. Decomposition is not appreciably retarded by N_2, A, He, O_2 and Hg up to 80 per cent added gas. H_2 retards the rate in proportion to the number of H_2^+ ions present.
6. The decomposition exhibits a less-than-unity temperature coefficient below 250°C. Above this temperature a small increase in rate exists at the higher pressures.
7. The M/N ratio lies between 0.5 and 1.0.
8. The mechanism of decomposition about the ions is discussed.

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CONDUCTIVITY MEASUREMENTS OF THORIUM AND OTHER JELLY-FORMING SYSTEMS

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In an important communication by Laing and McBain (1), it has been shown that sol and gel of one and the same substance are identical in their electrical conductivity, lowering of vapor pressure, refractive index, and some other minor properties. However, in the case of curds they found a marked drop in conductivity and osmotic activity. In previous publications from this laboratory, an attempt has been made to investigate various properties of inorganic jellies, for example, the viscosity and hydrogen-ion concentrations during the course of jelly formation (2), the syneresis of various jellies (3), the thixotropy (4), the changes in extinction coefficients (5), and the influence of various factors on the formation of jellies (6). In this communication, some observations have been made regarding the conductivity of some typical jellies such as thorium arsenate, thorium phosphate, thorium molybdate, ferric arsenate, and aluminum hydroxide.

EXPERIMENTAL

The jellies of thorium arsenate, thorium phosphate, and thorium molybdate were prepared by the method described by Prakash and Dhar (7). To thorium nitrate solution containing 12.5 g. of the salt in 250 cc. (23.54 g. of ThO_2 per liter), suitable concentrations of potassium arsenate, phosphate, or molybdate were added, and the changes in the conductivities during the course of gelation of these systems were investigated from time to time by the Hartmann and Braun roller bridge arrangement. The temperature was kept constant at 35°C. The observations have been recorded in table 1.

The results recorded in this table show that in the case of thorium arsenate, the mixture of thorium nitrate and potassium arsenate attains an equilibrium within thirty minutes, and after that the conductivity remains fairly constant up to the point of setting. As the opalescence increases, there is a slight decrease in the conductivity, the maximum decrease being obtained in the course of twenty-four hours when the jelly becomes almost opaque. The jelly on further aging, however, shows again an increase in the conductivity.

In the case of transparent jellies like thorium phosphate and thorium molybdate, when the mixture has once attained the equilibrium, the conductivity becomes constant. Even after the setting of the jellies, the conductivity does not change for a few hours. However, if the aging is allowed to continue, the conductivity also increases. The aging influence is less marked in the case of molybdate jelly.

TABLE 1

Conductivities of thorium jellies

Thorium nitrate solution = 10 cc.

Total volume = 12.5 cc.

	THORIUM ARSENATE 1 cc. of 18 per cent KH_2AsO_4	THORIUM PHOSPHATE 0.75 cc. of 20 per cent KH_2PO_4	THORIUM MOLYBDATE 1.5 cc. of 6 per cent K_2MoO_4
Time of setting..........	60 minutes	60 minutes	40 minutes
Nature of the jelly......	Opalescent jelly is obtained from clear solution. The opalescence increases continuously with time even after setting.	Opalescent mixture giving clear solution and finally a transparent jelly.	Opalescent mixture giving clear solution and finally a transparent jelly.
Time	Conductivity of the jellies in mohs × 10^{-3}		
0	4.255	3.710	2.385
5 min.	—	—	2.398
10 min.	—	3.635	—
15 min.	4.264	—	2.395
20 min.	—	3.616	—
25 min.	—	—	2.390
30 min.	4.297	—	—
40 min.	—	3.616	2.385
60 min.	4.297	3.616	2.385
100 min.	4.297	3.615	—
120 min.	4.285	—	—
180 min.	—	—	2.385
200 min.	—	3.654	—
260 min.	—	3.698	—
24 hrs.	4.142	3.855	2.385
48 hrs.	4.174	3.946	2.482
72 hrs.	—	—	2.451
96 hrs.	4.272	—	—

The influence of temperature on the conductivity of the above aged jellies has also been investigated. As the jellies were obtained by mixing the solutions of thorium nitrate with solutions of potassium arsenate, phosphate, or molybdate, the conductivities of these component solutions have also been measured at various temperatures. The concentrations of the solutions taken were the same as were necessary to give the above jellies. The results are given in table 2.

The results recorded in table 2 show that the temperature coefficients of the conductivities of thorium nitrate, potassium arsenate, potassium phosphate, and potassium molybdate are more regular, amounting to 2 per cent of the original conductivities at 35°C., as is usually found when Kohlrausch's expression is applied to electrolytes. The temperature coefficient of thorium arsenate jelly varies irregularly from 0.9 to 1.4 per cent of the original conductance; that of thorium phosphate is 1.54 per cent, and that of thorium molybdate 2 per cent of the original.

TABLE 2

Conductivities of component solutions

Thorium nitrate solution, 10 cc. diluted to 12.5 cc.; potassium arsenate, 18 per cent solution, 1 cc. in 12.5 cc. of water; potassium phosphate, 0.75 cc. of 20 per cent solution in 12.5 cc. water; potassium molybdate, 1.5 cc. of 6 per cent solution in 12.5 cc. water.

TEMPERATURE	CONDUCTIVITIES IN MHOS × 10^{-3}						
	Thorium nitrate	Potassium arsenate	Thorium arsenate jelly	Potassium phosphate	Thorium phosphate jelly	Potassium molybdate	Thorium molybdate jelly
degrees C.							
35	2.433	0.8463	4.272	0.1471	3.946	0.8245	2.450
40	2.673	0.9263	4.522	0.1595	4.238	0.9095	2.713
45	2.913	1.011	4.739	0.1731	4.484	0.9766	2.925
50	3.132	1.074	4.932	0.1879	4.834	1.066	3.178
55	3.370	1.165	5.217	0.2032	5.168	1.137	3.418
60	3.616	1.254	5.508	0.2153	5.467	1.226	3.659
Temperature coefficient (approximate)......	0.048	0.0163	0.049	0.0028	0.061	0.0166	0.048

TABLE 3

Changes in conductivity of ferric arsenate jelly on aging

TIME	CONDUCTIVITY
days	*mhos* × 10^{-3}
1	4.601
3	4.853
4	4.952
5	5.056

One thing which appears to be of interest is that the conductivities of the jellies of thorium arsenate and thorium phosphate are much greater than the total conductivities of the initial components. In the case of thorium molybdate, the conductivity of the jelly is slightly less than the additive conductivities of thorium nitrate and potassium molybdate. These results are discussed later on.

Ferric arsenate jelly

A positively charged sol of ferric arsenate, prepared by Holmes' method (8), containing 51.06 g. of ferric arsenate per liter and 0.028 *N* in chloride ions showed the following changes in conductivity on aging as it gained in the viscosity.

TABLE 4

Variation in conductivity with time

Conductivity of 10 cc. of solution with 2 cc. of water at 35°C. = 4.031 × 10^{-3}

TIME	CONDUCTIVITY
	mhos × 10^{-3}
0	5.865
10 min.	5.865
30 min.	5.865
2 hrs.	5.865
1 day	6.163

TABLE 5

Influence of temperature on the conductivity of ferric arsenate sol and jelly

TEMPERATURE	CONDUCTIVITIES IN MHOS × 10^{-3}	
	Sol	Jelly
degrees C.		
35	4.056	6.163
40	4.404	6.665
45	4.814	7.235
50	5.223	7.852
55	5.454	8.170
Temperature coefficient (approximate)..........	0.07 to 0.08	0.063 to 0.10

To 10 cc. of the sol of the first day were added 1 cc. of *N*/5 potassium chloride and 1 cc. of water. The jelly set in 30 minutes. The conductivity showed the variation with time given in table 4.

Thus there is no variation in the conductance during and after gelation. However, the jelly undergoes marked aging and gains in conductivity on keeping for a longer time.

The influence of temperature on the conductivities of 2 days old sol (10 cc. of sol with 2 cc. of water) and the above one day aged jelly is given in table 5.

On account of the presence of potassium chloride, the jelly is more conducting than the sol. The temperature coefficient of the sol is a little less than 2 per cent of the original conductance per degree, while in the case of the jelly, it is 1 to 1.4 per cent of the original.

Aluminum hydroxide jelly

An aluminum hydroxide sol was prepared by Crum's method. The sol dialyzed for seven days contained 10.48 g. of Al_2O_3 per liter. The jelly was obtained by adding 1 cc. of $N/10$ potassium chloride and 1 cc. of water to 10 cc. of the sol. From the clear sol, a transparent jelly accompanied with slight opalescence was obtained in the course of one hour. The changes with time during the gelation period and after are given in table 6. The conductivity of the sol previous to the addition of potassium chloride (10 cc. of sol + 2 cc. of water) was 1.120×10^{-4}. During the course of gela-

TABLE 6

Changes of conductivity with time during and after gelation period

Temperature = 35°C.

TIME	CONDUCTIVITY
	mhos $\times 10^{-3}$
0	1.477
10 min.	1.456
20 min.	1.456
60 min.	1.456
1 day	1.460
2 days	1.492
3 days	1.505

TABLE 7

Influence of temperature on the conductivity of aluminum hydroxide sol and jelly and of potassium chloride

TEMPERATURE	CONDUCTIVITIES IN MHOS $\times 10^{-3}$		
	Sol	Potassium chloride	Jelly
degrees C.			
35	0.1120	1.409	1.506
40	0.1247	1.539	1.655
45	0.1343	1.663	1.778
50	0.1455	1.794	1.914
55	0.1549	1.871	2.061
60	0.1675	—	2.213
Temperature coefficient (approximate)	0.00215	0.026	0.03

tion the conductivity remains fairly constant. However an increase is observed on aging.

The temperature influence on the conductivity of the following systems has also been investigated (see table 7):

1. 10 cc. of aluminum hydroxide sol mixed with 2 cc. of water.
2. 1 cc. of $N/10$ potassium chloride with 11 cc. of water.
3. 10 cc. of sol mixed with 1 cc. of $N/10$ potassium chloride and 1 cc. of water to give a jelly in 60 minutes. The jelly was allowed to age for three days before the temperature influence was studied.

Thus the conductivity of the jelly is almost additive of the conductivities of the sol and of the electrolyte. On the whole, the jelly is slightly less conducting than the components taken together. The temperature coefficient in all the three cases is per degree about 2 per cent of the original at 35°C.

DISCUSSION

The results recorded in the foregoing pages show the following facts:

The conductivity of thorium arsenate goes on decreasing with time as the opalescence increases up to a limit, when the jelly becomes completely opaque. Afterwards the jelly undergoes aging and the conductivity increases. The transparent jellies of thorium phosphate and thorium molybdate, once the equilibrium has been attained between the reactants, do not show any marked variation in the conductivities during the course of jelly formation. After a day or so, however, their conductivities begin to increase on aging. A similar behavior is observed with aluminum hydroxide and ferric arsenate jellies.

The conductivities of thorium arsenate and thorium phosphate jellies are greater than the conductivities of their initial components of the same concentrations, taken together. In the case of thorium molybdate, the conductance of the jelly is less than the additive conductances of thorium nitrate and potassium molybdate. The conductivity of aluminum hydroxide jelly is also slightly less than the additive values of aluminum hydroxide sol and the coagulant, potassium chloride.

The temperature coefficients per degree for the conductances of thorium nitrate, potassium arsenate, potassium phosphate, and potassium molybdate are about 2 per cent of the initial conductivities at 35°C. But the temperature coefficients of thorium arsenate and thorium phosphate jellies are considerably less. The graphs obtained by plotting conductivities against temperature are straight lines within the observed range (35°C. to 60°C.). The temperature coefficients of ferric arsenate and aluminum hydroxide sols are also about 2 per cent of the initial conductances. The temperature coefficient of ferric arsenate jelly is less than 2 per cent,— it is only 1 to 1.5 per cent of the conductance at 35°C. For aluminum hydroxide jelly, the temperature coefficient is about 2 per cent.

It has been observed by Dhar and coworkers (9) that the sols of ferric oxide, copper ferrocyanide, Congo red, arsenious trisulfide, silicic acid, etc., show a marked increase in the electric conductivity on aging. Gessner (10) found a decrease in the case of vanadium pentoxide sol. Roy and Dhar (11) observed that in most cases the light effect on colloids is merely an accentuation of the time effect, and consequently, on exposure to light, the conductivity increases. The stability of a sol is due to the stabilizing influence of similarly charged ions. Precipitates as well as sols, when aged, are found to have much less capacity of binding ions by adsorptive forces, so much so, that on aging some of the absorbed ions are set free. These free ions go to account for the increase in the observed conductivity.

The process of gelation is a specific case of coagulation where the uncharged particles instead of settling down after the formation of conglomerates, imbibe the dispersion medium. The coagulant adsorbs some of the ions from the free electrolytes of the medium, and consequently the total conductivity of a jelly system is a little less than the additive conductivities of the components, as has been found in the cases of aluminum hydroxide, ferric arsenate, and thorium molybdate jellies. When thorium nitrate is mixed with potassium molybdate to form the jelly, the reaction appears to proceed as follows:

$$Th(NO_3)_4 + 2K_2MoO_4 = Th(MoO_4)_2 + 4KNO_3$$

During the reaction, thorium molybdate comes down as a gelatinous mass, and thus some of the thorium and molybdate ions are removed from the field. In order to form the colloidal phase of thorium molybdate, some of the stabilizing ions are further adsorbed from the system. This accounts for the 25 per cent diminution in the conductance with respect to the additive values of the components in the case of thorium molybdate jelly.

The conductivities of thorium arsenate and thorium phosphate show a reverse effect. The conductivity of the jelly is much greater than the conductivities of the jelly-forming components taken together. This is due to the fact that while the normal potassium molybdate, K_2MoO_4, was used for the formation of molybdate jellies, the dihydrogen salts, KH_2AsO_4 and KH_2PO_4, were employed in the case of arsenate or phosphate jellies, where the reaction may be assumed to take place as follows:

$$Th(NO_3)_4 + 2KH_2AsO_4 = Th(HAsO_4)_2 + 2KNO_3 + 2HNO_3$$

From this reaction, it is clear that, owing to the formation of nitric acid, more ions are available after the reaction and consequently, in spite of the diminution due to the usual reasons, there is an increase in the conductivity of the system.

Though the conductivity of sols has been investigated by many workers, the temperature influence appears to have been neglected. The influence of temperature on the conductances of simple salts, according to Kohlrausch's classical expression, is linear within a sufficiently wide range and the temperature coefficients per degree approximate to about 2 per cent. The rise in the conductivity on the increase of the temperature is due to an increase in the mobility of the ions. The temperature coefficients of the jellies show an interesting feature. It appears that the increase in mobility of ions in jellies with rise of temperature is somewhat less than in the case of sols or solutions, and therefore the temperature coefficients are less than 2 per cent of the initial in the jellies. This point is exhibited in the case of thorium arsenate, thorium phosphate, and ferric arsenate jellies.

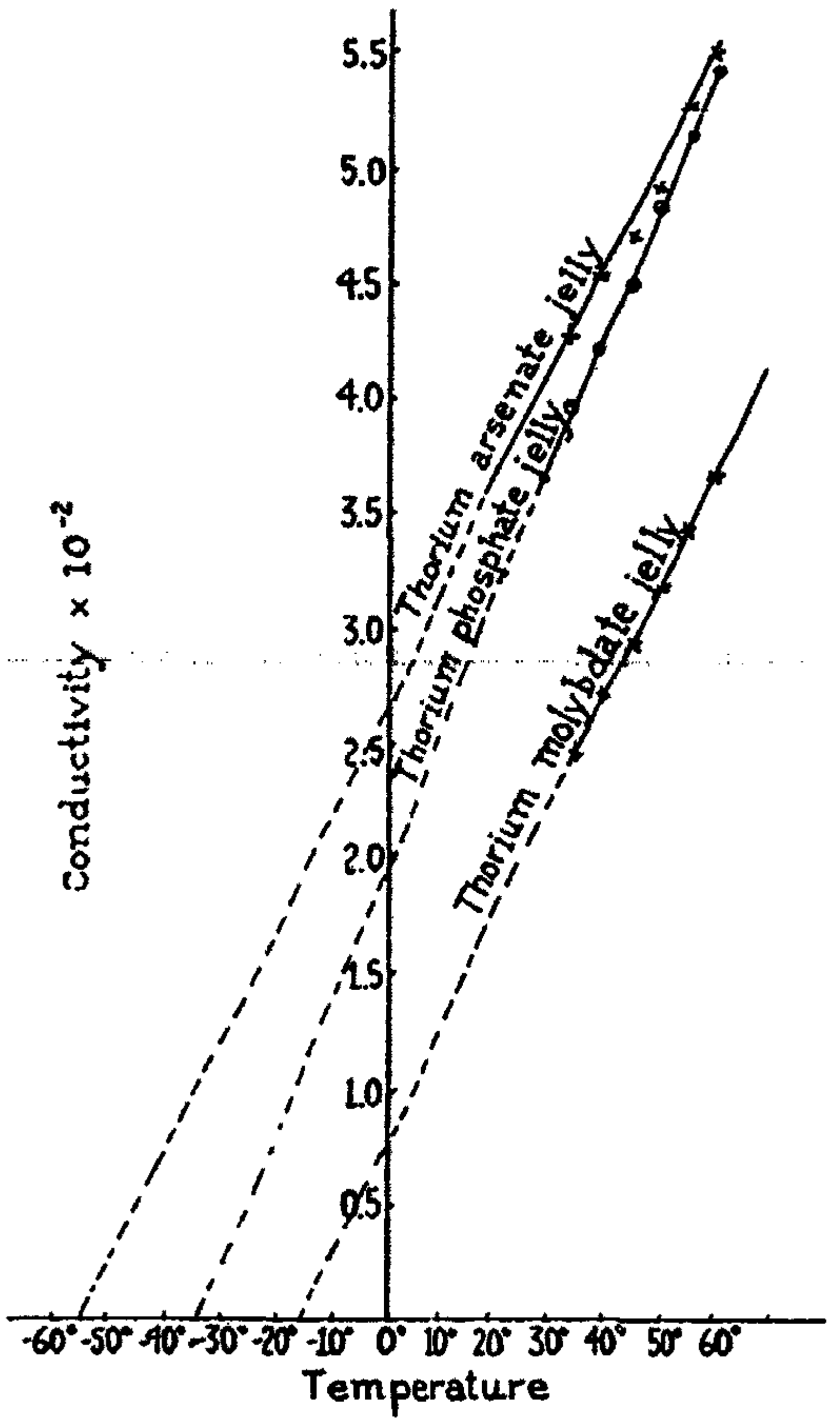

FIG. 1. THE INFLUENCE OF TEMPERATURE ON THE CONDUCTIVITY OF THORIUM JELLIES

One thing interesting to note is the deviation from the usual parallelism between temperature coefficients of conductance and the viscosity of the solvent medium. Ordinarily, it has been found that the conductivity of solutions becomes zero at temperatures near about −39°C. The jellies which we have investigated would have zero conductance at the temperatures given in table 8, as found by extrapolation (the relation between conductivity and temperature has been supposed to be linear down to the zero conductance).

The temperature at which water is supposed to possess an infinite viscosity is −34°C., a temperature at which it has almost no conductivity. When a sol undergoes setting, it gradually begins to gain in viscosity, and finally, it loses all its fluidity. From this, we might have expected a gradual decrease in conductivity too during the course of jelly formation,—a fact contrary to the observations. It shows that the decrease in the fluidity with the fall of temperature is materially very much different from the decrease during the course of jelly formation. It is an interesting fact that the water bound in a jelly offers no resistance to the ions present in the system.

TABLE 8

Temperatures of zero conductance of jellies

JELLY	TEMPERATURE OF ZERO CONDUCTANCE
	degrees C.
Thorium arsenate	−56
Thorium phosphate	−34
Thorium molybdate	−15
Ferric arsenate	−25
Aluminum hydroxide	−20

The conductivities of the jellies so far studied are mainly due to the electrolytic impurities, and in their comparison the effect of actual colloidal micelles is negligible. It is impossible to get an inorganic jelly without the free ions in the system, and as such, the conductivity is not a good property to throw much light on the nature of jellies. Laing and McBain got a difference of about one-fourth in conductivities of soap gels and curds. Even our completely opaque jellies, which may be called curds, do not show much marked decrease in the conductivity during the development of opalescence.

SUMMARY

1. The electrical conductivities of jelly-forming systems of thorium arsenate, thorium phosphate, thorium molybdate, ferric arsenate, and aluminum hydroxide have been investigated

2. It has been shown that once the equilibrium has been established between the jelly-forming components, the electrical conductivity becomes constant and no change is observed during the course of jelly formation or after the setting of the jelly. There is a slight decrease in the conductivity of thorium arsenate along with the development of opalescence until the jelly becomes completely opaque.

3. When the jellies are allowed to age for a number of days, the conductivity increases in all the cases.

4. The conductivities of thorium arsenate and thorium phosphate jellies are greater than the additive values for the conductivities of their components, because in their preparation the dihydrogen salts were used, which give rise to free nitric acid. In the case of thorium molybdate jelly, where a normal salt was used, the conductivity was less than that of the components. This is also the case with aluminum hydroxide.

5. The temperature influence on the conductivity of the jellies has also been investigated between 35°C. and 60°C. The relation between temperature and conductivity has been found to be linear within a wide range. The temperatures of zero conductance have been extrapolated.

6. The temperature coefficient for thorium molybdate and aluminum hydroxide jellies is about 2 per cent of the original at 35°C., while in the other cases, it is markedly less than 2 per cent (about 1 to 1.5 per cent).

The author expresses his indebtedness to Professor N. R. Dhar for his kind interest.

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PROMOTER ACTION IN THE CATALYTIC DECOMPOSITION OF SODIUM HYPOCHLORITE SOLUTIONS. IV[1,2]

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INTRODUCTION

The previous papers in this series (1, 2, 3) gave data for the decomposition of sodium hypochlorite in the presence of hydrated copper oxide, the catalyst, and also data for the decomposition of the hypochlorite when the catalyst was mixed with certain other catalytically inert oxides which have been designated as promoters (4). In the third paper of the series (3) the author pointed out that the promoter seemed to be effective in the formation and preservation of the active centers on the surface of the catalyst particles. It was also suggested that an ideally promoted catalyst is one in which each molecule of catalyst is separated from its neighbors in a definite way by a fixed number of molecules of promoter, possibly arranged in a definite pattern. This paper gives additional data showing the promoter effect of certain oxides and other insoluble substances on the catalytic decomposition of hypochlorite and in addition shows that there is no apparent simple relation between the crystal structure of the promoters and their activity.

EXPERIMENTAL

Materials and apparatus

The hypochlorite, catalyst, and promoters were prepared as described previously (3). A shaker apparatus, similar to the one originally designed by Walton, was used in following the reaction (5).

Experimental procedure

The procedure followed in these experiments was essentially the same as that outlined in previous papers. However, the details were modified somewhat in those cases where it was necessary to precipitate the catalyst

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[1] Contribution No. 40 from the Chemical Laboratory of the University of Utah.

[2] Part of the experimental results presented in this paper were reported to the Chemical Division of the American Association for the Advancement of Science at the Pasadena Meeting, June, 1931.

as oxide and the promoter as sulfate, carbonate, or other insoluble substance. For example, when it was desired to study the promoter effect of barium sulfate in the presence of the catalyst, barium and copper ions were introduced into the reaction flask and then at the proper time a solution containing the hypochlorite and the sulfate ions was introduced through the side-neck of the flask. This procedure insured the coprecipitation of the two insoluble substances.

RESULTS

In the experiments recorded in this paper the substances designated as "promoters" (when used in the absence of the catalyst) had no effect on the velocity of the reaction. Not only did the authors avoid using mixed catalysts for this study but they also selected a catalyst of moderate activity. In this way the promoter effect of the catalytically inert substances was more apparent.

TABLE 1

*Velocity of the reaction as related to the ratio of promoter atoms added to one atom of catalyst**

CADMIUM AS CdO		CALCIUM AS CaO		MERCURY AS HgO	
Ratio	$K \times 10^4$	Ratio	$K \times 10^4$	Ratio	$K \times 10^4$
0.00	10	0.00	10	0.00	10
0.07	30	0.10	14	0.70	48
0.14	132	0.265	35	1.4	80
0.208	205	0.35	40	2.1	108
0.278	192	0.52	46	2.8	176
0.348	171	0.70	43	3.48	126
0.417	142	0.87	40	4.15	112
0.70	100	1.30	33	5.55	87
1.04	55	1.72	26	7.1	60
1.72	42	2.61	14		

* Hydrated copper oxide is the catalyst in all cases.

The results are summarized in tables 1 to 3 and shown graphically in figures 1 and 2. The rate of the reactions is expressed by means of the unimolecular constant ($K \times 10^4$) and by giving the volume of oxygen liberated at various time intervals.

DISCUSSION OF RESULTS

The data given in table 1 and presented graphically in figure 1 show the effect of increasing amounts of promoters on the rate of the catalyzed reaction. Further, they show that the maximum promotion is obtained, not at a definite ratio of promoter to catalyst atoms, but rather at various ratios, depending upon the promoter used. With each promoter studied, it is apparent that its effect becomes negligible as the ratio of promoter to catalyst becomes high. This may be explained, as suggested in the previous paper, by assuming that the active centers of the catalyst are covered at the higher ratios. On the other hand, the fact that maximum promotion comes at various ratios of catalyst to promoter seems to indicate that the promoter effect is due to a physical spreading out of the catalyst (perhaps on a foundation of promoter molecules), rather than to any definite arrangement (crystal pattern) of catalyst and promoter as was suggested in the third paper of the series.

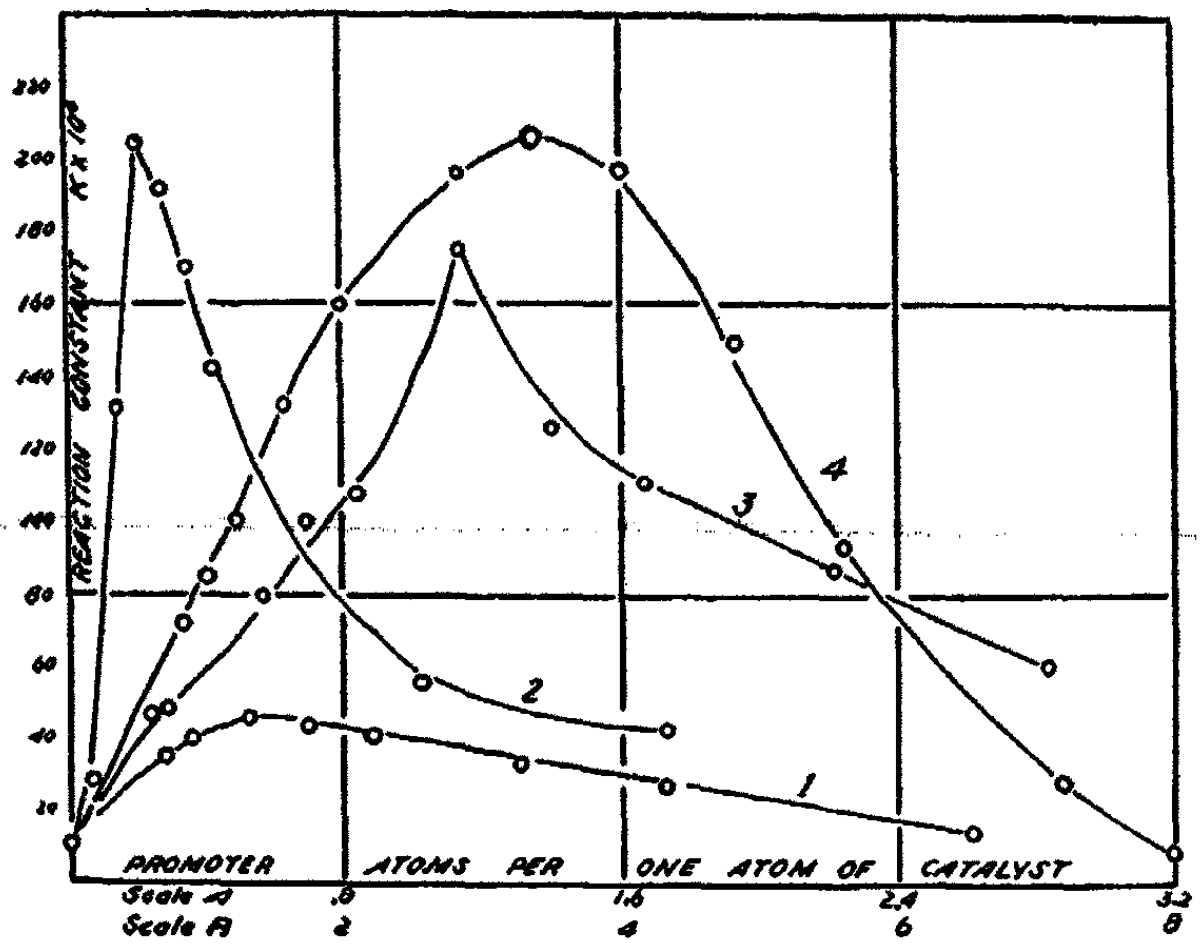

FIG. 1. CURVES SHOWING THE PROMOTER EFFECT OF VARIOUS OXIDES ON THE COPPER OXIDE CATALYSIS OF HYPOCHLORITE SOLUTION

Curves 1 and 2 are plotted to scale A. Curves 3 and 4 are plotted to scale B. Curve 1, calcium oxide; curve 2, cadmium oxide; curve 3, mercuric oxide; curve 4, magnesium oxide. Data for curve 4 were taken from the third paper of this series.

Additional data which point in the same direction are given in tables 2 and 3 and shown graphically in figure 2. It will be observed that there is no apparent simple relationship between the crystal structure of the promoter and its activity. It appears that many insoluble substances can serve as a promoter if coprecipitation of the catalyst and promoter is attained (see numbers 7 and 8 in table 2).

That the mechanical spreading of a catalyst by an inactive substance results in a "promoter effect" seems to be clearly shown by the above data.

TABLE 2

Promoter action of various insoluble substances on the copper oxide catalysis of sodium hypochlorite solution

NO.	RATIO OF CATALYST TO PROMOTER		CUBIC CENTIMETERS OF OXYGEN LIBERATED AT VARIOUS TIME INTERVALS											
	Catalyst	Promoter												
1	CuO	None	Minutes......	3	12	20	30	40	50	60	80	100		
			cc. O_2........	0.35	0.7	1.0	1.3	1.6	1.9	2.25	2.85	3.42		
2	CuO	BaO	Minutes......	3	6	9	12	15	21	24	27	30	35	
	1 to 1.39		cc. O_2........	1.45	2.5	3.8	4.4	5.3	6.9	7.6	8.3	8.8	9.7	
3	CuO	BaC_2O_4	Minutes......	3	6	9	12	15	18	21	24	27		
	1 to 1.39		cc. O_2........	1.6	2.7	3.6	4.6	5.7	6.6	7.7	8.7	9.65		
4	CuO	CaC_2O_4	Minutes	3	6	9	12	15	21	24	30	35	40	50
	1 to 1.78		cc. O_2........	1.2	1.8	2.2	2.5	2.8	3.3	3.5	3.9	4.1	4.4	5.0
5	CuO	$BaCO_3$	Minutes.	3	6	9	12	18	21	27	35	40	45	50
	1 to 1.39		cc. O_2........	2.1	2.4	2.7	2.9	3.3	3.5	3.83	4.35	4.6	4.8	5.1
6	CuO	$CaCO_3$	Minutes......	5	10	15	20	25	30	40	50	60	70	85
	1 to 1.78		cc. O_2........	0.3	0.4	0.5	0.7	0.8	1.0	1.35	1.78	2.3	2.9	4.0
7	CuO*	$BaSO_4$	Minutes......	3	6	9	12	18	24	30	40	50	60	
	1 to 1.39		cc. O_2........	0.3	0.5	0.6	0.7	0.9	1.05	1.23	1.53	1.83	2.1	
8	CuO†	$BaSO_4$	Minutes......	3	6	9	12	18	24	30	40	50	60	
	1 to 1.39		cc. O_2........	1.7	2.3	2.6	2.8	3.1	3.45	3.73		4.6		

* The copper oxide and barium sulfate were precipitated separately and then mixed.

† The copper oxide and barium sulfate were coprecipitated.

TABLE 3

The relationship of crystal structure of certain oxides to their promoter activity in the copper oxide catalysis of hypochlorite*

PROMOTER	$K \times 10^4$ AT MAXIMUM PROMOTION	CRYSTAL SYSTEM	STRUCTURE TYPE
Copper oxide (catalyst)	7	Triclinic	NaCl (distorted)
Magnesium oxide†	207	Cubic	NaCl
Cadmium oxide	205	Cubic	NaCl
Calcium oxide	43	Cubic	NaCl
Barium oxide	75	Cubic	NaCl
Mercuric oxide	176	Orthorhombic	HgO
Ferric oxide‡	99	Hexagonal	Fe_2O_3
Barium sulfate	19	Orthorhombic	$BaSO_4$
Calcium carbonate	20	Orthorhombic	KNO_3
Calcium oxalate	21	No data	
Barium oxalate	76	No data	
Barium chromate	7	No data	

* Crystal structure data were obtained from The Structure of Crystals, by Wyckoff, 2nd edition. The Chemical Catalog Co., New York (1931).

† Data from the third paper of this series.

‡ Data from the second paper of this series.

However it does not seem reasonable to suppose that such large increases in reaction rate produced by such small quantities of promoter can be completely accounted for in this manner. It seems apparent that some other explanation still is to be sought.

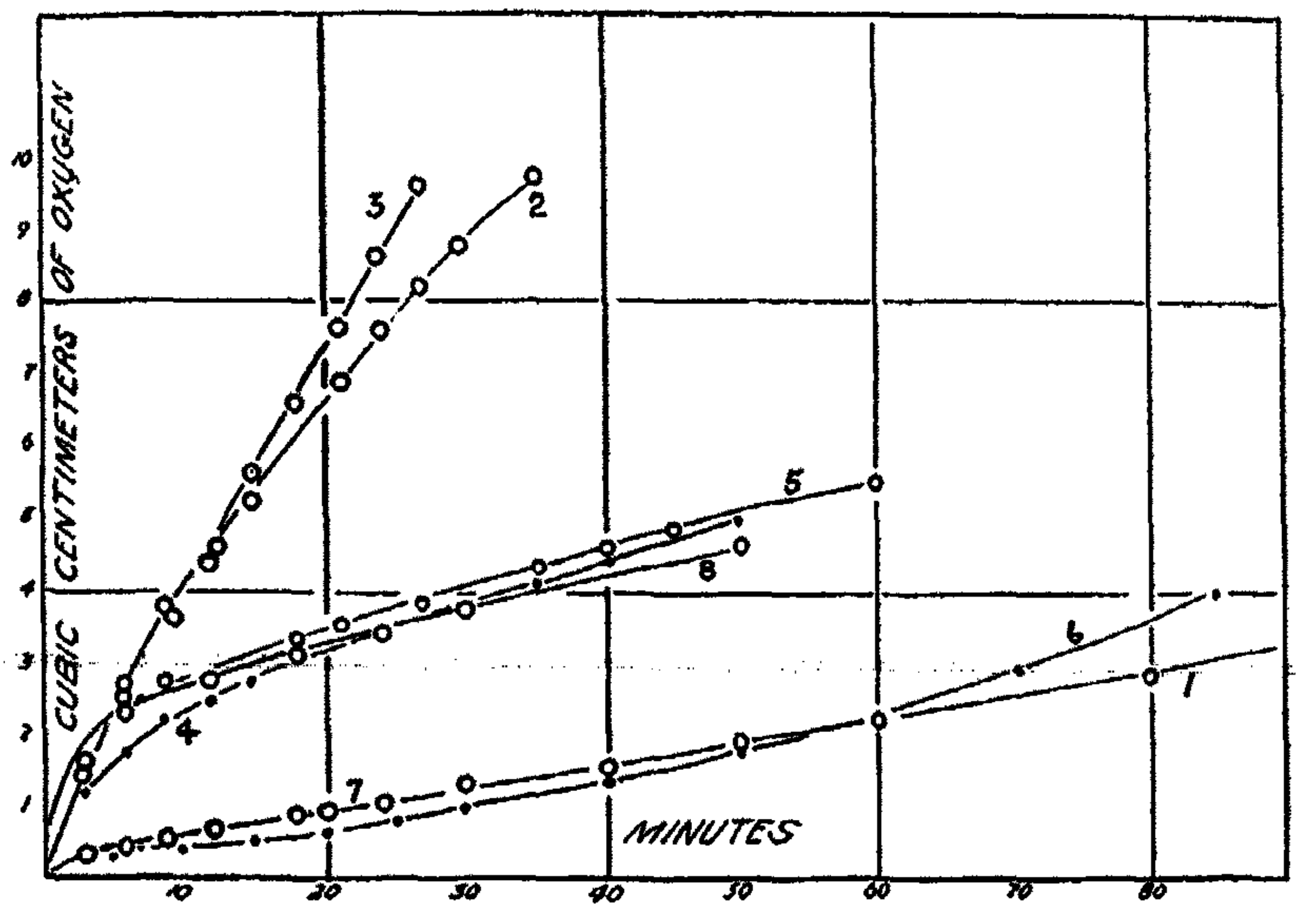

FIG. 2. CURVES SHOWING THE PROMOTER EFFECT OF VARIOUS INSOLUBLE SUBSTANCES ON COPPER OXIDE CATALYST

1, No promoter; 2, barium oxide; 3, barium oxalate; 4, calcium oxalate; 5, barium carbonate; 6, calcium carbonate; 7, barium sulfate precipitated separately; 8, barium sulfate coprecipitated.

SUMMARY

1. The promoter effect of several oxides and other insoluble substances has been determined in the copper oxide catalysis of sodium hypochlorite solution.

2. There seems to be no simple relationship between the crystal structure of a promoter and its activity.

3. Promoter action seems to be due in part to a mechanical spreading of the catalyst.

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THE ATOMIC MASS OF SODIUM. II

THE SODIUM CHLORIDE–SILVER RATIO

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The present study of the sodium chloride–silver ratio was designed to develop and test a new general method for the determination of atomic mass ratios.

PURIFICATION OF REAGENTS

The reagents used in this work were purified by methods (1) which were shown to be adequate by suitable tests. The general criterion of acceptable purity for any reagent was that the amount used in a single analytical system or 1500 g. of standard solution would introduce no silver or chloride impurities equivalent to more than 0.005 mg. of silver. Simple and sensitive nephelometric tests (2) made it possible to fulfill this condition with certainty.

Sodium chloride

The sodium chloride was obtained from 500 g. of Merck's C. P. reagent. It was precipitated successively three times from saturated solution with central fractions of hydrogen chloride distilled from C.P. concentrated hydrochloric acid, fused in platinum, and then crystallized three times from pure water. Before each treatment the solution was filtered through a Munroe crucible, and the recovered cyrstals were always dried in a centrifuge at 1500 r. p. m. for fifteen minutes. Uniform initial and final fractions were rejected in each of the six precipitations or crystallizations. The work was conducted under glass covers to eliminate dust, and the solutions came into contact only with platinum dishes.

The 107 g. of material obtained after the sixth crystallization was separated into five fractions by crystallization from water. As each of the fractions was obtained it was redissolved in water and passed through a platinum Munroe crucible directly into a platinum receiver. The solution was evaporated in a 150-cc. platinum dish, and the dry salt was transferred with a spatula to covered platinum cups in a vacuum desiccator. Each

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of the platinum implements was weighed just before and after handling each fraction. The maximum possible extent and distribution of the platinum impurities was thus determined with precision (see table 1). Since only part of the platinum accidentally scraped from the dish and spatula was transferred with the samples, it is safe to say that the average error due to platinum impurities in the sodium chloride is well below the maximum platinum content of 1 part in 270,000.

TABLE 1

Platinum impurities in sodium chloride

FRACTION NO.	WEIGHT	MILLIGRAMS OF PLATINUM IMPURITIES FROM			
		150-cc. dish	Spatula	Receiver	Filter
	grams				
1	26	0.04	0.00	0.00 in all five	0.02 in all five
2	26	0.06	0.00		
3	18	0.04	0.00		
4	25	0.07	0.03		
5	12	0.12	0.02		

Neutrality of sodium chloride

It is not possible for well-dried, vacuum-desiccated sodium chloride to hydrolyze to any great extent during fusion. Samples of the sodium chloride fused in air or nitrogen by the method hereinafter described were shown to be neutral in ordinary tests with indicators. The possibility of slight hydrolysis during fusion is now being studied in more detail with the cell: tungsten | tungsten oxide | fused NaCl (satd.) | unfused NaCl (satd.) | tungsten oxide | tungsten.

Containers

The various Pyrex flasks and beakers used in the analyses were all examined for cracks by the sensitive phenolphthalein-sodium hydroxide test. This was an important precaution, since almost invisible cracks were found in several cases. All vessels were cleaned by washing in order with soap and water, cleaning solution, concentrated aqua ammonia, nitric acid, and water. It was noticed that the removal of silver chloride from glass vessels with ammonia leaves on the walls a film of some material containing an excess of silver over chloride. This observation has a bearing on many points of technique in nephelometric work with silver chloride.

THE ANALYSES

The analytical weighings and transfers of material were made with precautions which make them accurate to about 0.01 mg. For each weighing the air density was determined from temperature, pressure, and psychrometric observations, and vacuum corrections were applied on the basis of the known volumes of the weights and densities of the materials. Weighings were made by the method of substitution, on a No. 10 Troemner balance sensitive to 0.01 mg. with a load of 20 g. It may be noted that 0.01 mg. of silver, silver chloride, sodium chloride, or the equivalent in suitably diluted solutions, is distinctly visible; it is possible to be reasonably certain that carefully controlled weighings and transfers are quantitative to this extent. In the few cases in which larger quantities of the materials may be present in invisible films, the procedures insure the same degree of certainty.

Titration analyses

For each analysis a 5.4 to 5.5 g. sample of sodium chloride was fused in a weighed 20-cc. platinum crucible in an electric furnace, after desiccation in vacuum over fused potassium hydroxide for at least three days. The covered crucible was completely inclosed in a covered quartz crucible surrounded by a quartz muffle. The crucible and contents were raised to 810°C. over about twenty minutes, then held at 810° to 860°C. for five to thirty minutes. After the loaded crucible had cooled sufficiently, it was returned to a desiccator, and cooled completely before weighing.

By the use of a suitable counterpoise crucible, the weights of the empty or charged crucible could be duplicated to 0.01 mg. in successive weighings, made at widely separated times. In no case was there any evidence of gain of moisture from air of low or moderate humidity in which all weighings were made. The weighed crucible containing the fused salt was placed in a Pyrex beaker with a "dripless" lip, and the salt was dissolved in 500 cc. of pure water. The resulting solution was transferred to the analytical system without delay.

The thoroughly washed crucible was dried in a porcelain electric furnace at 300°C., and the rechecked difference between the weights of the crucible and counterpoise served as the initial value in the next analysis. The volatility and solubility of the platinum crucible under these conditions was very small. In nine analyses the crucible used in fusing the sodium chloride lost only 0.07 mg., which was distributed as a uniform steady loss. A quartz crucible was used for the sample which was fused in nitrogen carrying a small amount of hydrogen chloride.

The purified silver, in the form of fused buttons and electrolytic crystals, was prepared for weighing by heating to 500°C. in an evacuated quartz tube, and was kept in a desiccator over fused potassium hydroxide. The silver was weighed directly on the balance pan, and handled with ivory-tipped forceps and a watch glass. Successive weighings of the same silver, involving transfer to the watch glass and return to the pan, could be duplicated to 0.01 mg. A satisfactory check consisted in making the substitutions in the order: weights-silver-weights. For each analysis silver approximately 1.8454 times the predetermined weight of the sodium chloride was taken for exact weighing. Crystals made up only 2 to 8 mg. of the total weight of silver. The silver was dissolved in 1:1 nitric acid, using 76.0 cc. of 7.57 molar nitric acid per 10.00 g. of silver, with precautions to avoid mechanical loss. The solution was diluted to 500 cc. before transferring it to the analytical system, at room temperature.

The general scheme of analysis, designed to obtain evidence on several points of interest, is shown in table 2. In each case one of the 500 cc. solutions was added to the other at the rate of 4 cc. per minute. The latter solution was contained in a weighed 3-liter glass-stoppered Pyrex Erlenmeyer flask, which was rotated repeatedly during the addition. The transfer apparatus consisted of a 250-cc. tall-form funnel with a stirring rod ground into the top of the stem and slotted to permit the drop by drop addition of solution to the large flask. The rod extended beyond the flared rim of the funnel, and was bent to form an obtuse angle a little above the rim. It could be removed to permit the rapid addition of wash water. The transfers were made under glass covers to avoid dust impurities.

TABLE 2

Scheme of analysis

$NaCl$ added to $AgNO_3$				$AgNO_3$ added to $NaCl$			
Fraction No.	Fused in	Time fused	Maximum temperature	Fraction No.	Fused in	Time fused	Maximum temperature
		minutes	*degrees C.*			*minutes*	*degrees C.*
1a	Air	20	830	1b	Air	5	820
2a	N_2	30	830	2b	N_2	30	830
3a	Air	5	820	3b	$HCl-N_2$	15	860
4a	Air	10	820	4b	Air	10	810
5a	Air	10	810	5b	Air	5	810

After addition of the wash waters, the system was made up with water, by weighing on a large balance, to contain 1520.7 g. of solution per 10.0000 g. of silver (7.8796 g. of sodium nitrate). Each supernatant analytical solution thus had the same composition as the solutions used in previous work (3) on the end point of the sodium chloride–silver titration. The analytical system was brought to equilibrium at 0°C. and portions of the supernatant liquid were withdrawn and filtered at this temperature, and later analyzed in the manner described in detail in the above-mentioned report, by nephelometric comparison (at room temperature) with exactly similar standard solutions containing measured amounts of silver and chloride. A number of these standards, each containing 7.8796 g. of sodium nitrate and 28.46 g. of hydrogen nitrate per 1520.7 g. of solution, were made up to cover a short range of silver and chloride concentrations in the end point region. This range could be narrowed as desired, either by weighing out the original samples of sodium chloride and silver in more nearly equivalent amounts, or by making additions as described below, and also by allowing ample time for the complete coagulation of the colloidal silver chloride in the analytical systems.

After preliminary analyses of the supernatant analytical liquid, its silver and chloride contents were adjusted to approximate equality in the usual manner, by the addition of dilute standard silver nitrate or sodium chloride solutions. The end point of the titration was then determined by four to eight sets of nephelometric analyses made over a period of several days with two or three independently prepared standards. The average difference in the measured silver and chloride concentrations located the end point directly, with an uncertainty equivalent to only about 0.02 mg. of silver. In several cases further adjustments were made, and the end point determinations were repeated. It may be noted that *when the liquids were near the correct end point*, small measured additions of silver nitrate or sodium chloride agreed quantitatively with the resulting changes shown in the composition of the supernatant liquids by the standard solution tests, within about 0.02 mg. of silver or its chloride equivalent.

In the analyses of samples 2b, 4a, and 4b, the end point was also determined by potentiometric analyses made at 0°C. with the cells:

Ag | AgCl | Analytical solution | Standard solution | AgCl | Ag
Ag | Analytical solution | Standard solution | Ag

In these measurements, in order to eliminate errors due to liquid junction potentials, it was necessary to make slight adjustments in the nitric acid concentration of the analytical solutions. Exact predetermination of the nitric acid concentration was prevented by the small variations in the amount of nitrogen oxides retained during solution of the silver. This point presented no difficulty, as the necessary adjustments could be made with precision after titration of test portions of the solutions with standard alkali.

The differences in the silver and chloride concentrations in each of the supernatant liquids, as found in the potentiometric analyses, gave the same end points as the corresponding nephelometric analyses. The solubility values found were uniformly a little lower for the potentiometric experiments. It seems likely that identical results would be obtained in both cases by allowing ample time for the complete coagulation of the colloidal silver chloride. For the sake of uniformity the solubility values given in subsequent tables are the nephelometric values, which must be preferred in estimating silver and chloride in rejected liquors and washings.

Gravimetric analyses

A new technique for the collection and estimation of silver chloride was also studied. In developing this gravimetric procedure, every effort was made to minimize or eliminate minor corrections, in recognition of the fact that a multiplicity of corrections increases rather than diminishes constant errors.

At the completion of each titration analysis the supernatant liquid remaining was poured into a weighed 600-cc. beaker, then decanted through an accurately weighed Munroe crucible while still at about 0°C. The bulk of the precipitate was transferred to the beaker with the last of the liquid. The flask was inverted in a ring over the beaker and the last visible traces of silver chloride were removed with the aid of a wash-bottle with an S-shaped nozzle, filled with a portion of the cold, filtered, supernatant liquid. The crystals in the beaker were drained, and the filtered supernatant liquid was collected and later analyzed for silver and chloride by comparison with standard solutions having the same composition, in the nephelometer. The liquid retained by the silver chloride was estimated by weighing the beaker and its contents to the nearest 0.5 g.

The silver chloride was washed with ten 25-cc. portions of dilute acid containing in all 1.0 cc. of 7.57 molar nitric acid, then with four 25-cc. portions of pure water, with the last of which it was transferred to the Munroe crucible. A perforated platinum plate was used to shield the filter mat. The silver chloride was dried at a temperature increased from 80° to 110°C. during four hours, in a porcelain electric furnace, then heated at 300°C. for twelve hours before weighing. The crucible and contents were again heated at 300°C. for six hours and weighed a second time. In ten experiments the loss during the second heating averaged 0.014 mg., and never exceeded 0.03 mg. Satisfactory proof of the constancy in weight of the Munroe crucible during these operations was obtained by removing the bulk of the precipitate, dissolving any adhering silver chloride in aqua ammonia, and washing in proper sequence with water and nitric acid, before drying and reweighing the crucible. Under these conditions the difference in weight between the crucible and counterpoise could be rechecked to about 0.02 mg. When such rechecks are desired, the crucible should not be inverted during washing, as loose particles sometimes develop on the top of the mat.

No "loss on fusion correction" for the silver chloride was made. Hönigschmid and Chan (4) have shown that the loss on fusion after drying silver chloride at 300°C. is so small as to be of doubtful significance.

The nitric acid–water washings of the silver chloride were preserved and later made to 500 cc. with the aqua ammonia–nitric acid–water washings. The latter washings consisted of 50.0 cc. of 1.5 molar ammonium hydroxide prepared by distilling concentrated C. P. aqua ammonia into water in a Pyrex apparatus, 25.0 cc. of 7.57 molar nitric acid, and water, used in proper sequence. Care was taken not to acidify the ammonia solution before the final combination of washings. These washings covered all surfaces which might have retained silver chloride, in the following vessels: (1) the pipette and filter used in withdrawing and filtering the nephelometric test portions, (2) the containers used for storing the washings, (3) the transfer beaker and stirring rod, (4) the receiving flask, (5) the 3-liter analysis flask, and (6) the porcelain interior of the electric furnace.

The silver and chloride in the combined washings were estimated by nephelometric comparison of 20.0-cc. test portions with equal volumes of standard solutions. The standard solutions were made up in 500 cc. amounts, each containing 26.0 cc. of 7.57 molar nitric acid, 50.0 cc. of 1.5 molar ammonium hydroxide, solution to correspond to the weighed supernatant liquid retained by the silver chloride, and measured equivalent amounts of silver and chloride. The nitric acid and ammonia solutions were equal aliquot portions of the same reagents used in the washings; the other solution was a quantity of one of the standard solutions used in the end point tests, corrected for its silver and chloride content. These standards thus had precisely the same composition as the combined washings, as the silver and chloride content could be adjusted to the desired value after one approximation. Under the conditions described above, analyses made in duplicate or triplicate agreed within 0.02 mg. It should be emphasized that it is only by such systematic regulation of conditions that the anomalies usually observed in these tests may be eliminated.

Analyses of solutions

In recognition of the possibility that abnormalities due to adsorption effects might be revealed thereby, all of the various supernatant liquids and washings from the precipitated silver chloride were analyzed both for their silver and chloride contents. Each of the values given in the summary of these analyses (table 3) is the mean of at least three measurements made by the standard solution method. On the average the individual values may be trusted to about 0.02 mg. The chloride concentrations in the table are multiplied by the factor Ag/Cl. Compared with normal solubility values, most of the values given in the first two columns of the table are a little too high. It would have been impractical to wait for the complete coagulation of the colloidal silver chloride in these experiments, although it was recognized that this would slightly increase the precision of the end point measurements. The single low value represents a solution frozen, melted, and analyzed while held at 0°C., under conditions preventing it from attaining complete saturation.

TABLE 3

Summary of analyses of solutions

SAMPLE NO.	SOLUTION NEAR END POINT, 0°C.		SAME AFTER SEPARATION		COMBINED WASHINGS	
	Chloride	Silver	Chloride	Silver	Chloride	Silver
	mg./liter	*mg./liter*	*mg./liter*	*mg./liter*	*mg./600 ml.*	*mg./600 ml.*
1a	0.56	0.50	0.80	0.76	0.99	1.00
1b	0.73	0.66	0.78	0.97	0.44	0.43
2a	0.69	0.69	0.77	0.76	0.37	0.37
2b	0.73	0.67	0.79	0.74	0.40	0.40
3a	0.73	0.71	0.79	0.75	0.40	0.40
3b	0.71	0.70	0.72	0.74	0.51	0.51
4a	0.65	0.71	0.72	0.78	0.33	0.33
4b	0.71	0.70	0.95	0.91	0.48	0.49
5a	0.66	0.61	0.77	0.82	0.48	0.44
5b	0.75	0.68	0.86	0.76	0.37	0.39

DISCUSSION OF RESULTS

The present research was designed for the development and testing of new procedures for use in the determination of atomic mass ratios, and attention is confined mainly to this aspect of the experimental results.

Titration analyses

The pairs of analyses made with uniform samples of fractions 1, 2, 4, and 5 give values for the sodium chloride-silver ratio which show that the new analytical method is an unusually *precise* one. The average deviation of the individual ratios from the respective means is only 3 parts in 540,000. There is no discrepancy between the known precision of the separate steps of the analytical procedure and the experimentally observed precision of the entire procedure. Such a discrepancy might have been expected if the silver or sodium chloride was not uniform, or if the composition of the silver chloride precipitates with respect to silver and chloride was not definite.

The results obtained for fraction 3 were excluded from the above considerations by the predetermined analytical scheme. The analysis of sample 3b shows that some of the hydrogen chloride dissolved in the molten sodium chloride was not removed when the material was cooled in a current of nitrogen. Other portions of the sodium chloride, fused under the same conditions as sample 3b, but not analyzed, gave an acid reaction with indicators when dissolved in water. The high sodium chloride-silver ratio obtained for sample 3a is puzzling. The only reason to believe that the result does not represent a correct analysis of the fraction is to be found in the analyses of the adjacent fractions.

It was recognized that any impurities in the sodium chloride obtained in the sixth crystallization would tend to concentrate in fraction 5, and that the analyses of this fraction could have no standing as determinations of the sodium chloride–silver ratio. However, these analyses accomplish their main purpose by showing that even the residual liquor from which the other fractions were crystallized was remarkably pure.

TABLE 4

Summary of analyses

NO.	NaCl IN VACUUM	Ag IN VACUUM	NET Ag ADDED	FINAL Ag EXCESS	TOTAL Ag ⇔ NaCl	RATIO NaCl:Ag
	grams	*grams*	*mg.*	*mg.*	*grams*	
1a	5.48994	10.13092	1.45	−0.09	10.13246	0.541817
1b	5.43976	10.03832	1.70	−0.11	10.03981*	0.541819
2a	5.48976	10.13054	1.69	±0.00	10.13223	0.541812
2b	5.47090	10.09582	1.33	−0.09	10.09724	0.541821
3a	5.42144	10.00451	0.48	−0.03	10.00502	0.541872
3b	5.4360	10.0314	2.54	−0.02	10.0340	(0.54176)
4a	5.59192	10.31920	1.53	+0.09	10.32064	0.541819
4b	5.43087	10.02204	1.46	−0.02	10.02352	0.541813
5a	5.51668	10.17998	2.22	−0.08	10.18218*	(0.541798)
5b	5.42755	10.01596	1.71	−0.11	10.01778	(0.541792)

NO.	DRY AgCl IN VACUUM†	AgCl IN ALL SUPERNATANT LIQUIDS	AgCl IN COMBINED WASHINGS	TOTAL UNFUSED AgCl	RATIO AgCl:Ag
	grams	*mg.*	*mg.*	*grams*	
1a	13.45877	1.56	(1.32)	13.46165	(1.32857)
1b	13.33790	1.44	0.59	13.33993	1.32870
2a	13.46031	1.51	0.49	13.46231	1.32866
2b	13.41347	1.52	0.53	13.41552	1.32863
3a	13.29126	1.48	0.53	13.29327	1.32866
3b	13.3286	1.44	0.68	13.3307	1.3286
4a	13.71081	1.38	0.44	13.71263	1.32866
4b	13.31536	1.63	0.64	13.31763	1.32864
5a	13.52674	1.45	0.64	13.52883	1.32868
5b	13.30805	1.63	0.49	13.31017	1.32866

* Corrected as noted in text.

† Corrected for minute amounts of sodium chloride added in adjusting the solutions to the end point.

In discussing the *accuracy* of the new method, it is important to consider the evidence concerning the composition of precipitated silver chloride, which is the only factor in this type of precipitation analysis over which the analyst has no direct control. At other points the methods available for checking the accuracy of the procedures and the purity of the materials are adequate. For the titration method, the problem here involved is considerably simplified by the fact that it is only the silver nitrate or sodium chloride adsorbed or otherwise included by the precipitate that need be considered. Moreover, if adsorption or occlusion is an important factor in determining the composition of the precipitate, silver chloride coagulated in a solution containing excess of sodium chloride and that formed in excess of silver nitrate should differ markedly, and the difference might be expected to appear in the measured sodium chloride–silver ratios. In the present experiments, the results obtained by reversal of the order of precipitation, in pairs of analyses in which uniform samples of sodium chloride and silver were used, indicate that no such adsorption or occlusion occurred. Further evidence to support this conclusion is found in the fact that the removal of successive layers from the precipitates by warming and washing showed no anomalies, when the end point adjustments were properly made.

The above remarks apply only to experiments in which the silver chloride was in contact with solutions extremely close to the correct end point. In other cases, with either silver nitrate or sodium chloride in excess, some of the excess material may be taken up by the precipitate. It follows that under certain conditions, depending on the manner in which the end point is approached, the silver and chloride content of the supernatant liquid cannot be trusted to show the difference in the amounts of silver and chloride in the system.

An example of such a case is found in the analytical data for sample 1b. The change in the silver content of the supernatant liquid indicates that silver was in excess in the precipitate during the end point determination, and that it was later ejected by the precipitate. The ejection must have occurred either during the warming which accompanied the separation of the supernatant liquid or in the period of standing which preceded the separation. Proper correction was made for the excess silver found in the 1220 cc. of separated liquid. Reference to the measured ratios shows that the silver chloride expelled the excess silver to return to the same composition as other precipitates which were never in contact with a solution containing excess silver. This behavior offers additional evidence of the definite composition of the original silver chloride precipitates. It also indicates that adsorbed or occluded material is not held very firmly, an observation which would appear to explain the absence of irregularities due to reversal of the titration for the pairs of samples. It may be noted that the analysis of sample 1b was the first to be completed; in subsequent analyses the adjustments to the end point were made in a manner calculated to avoid the difficulty.

Gravimetric analyses

The silver chloride–silver ratios found in the gravimetric analyses show in a general way that the silver and sodium chloride used in this work were highly pure. It may also be inferred that the amount of sodium nitrate retained by the precipitates was extremely small. The value obtained for sample 1a is open to suspicion for the reason that the combined washings were found to be saturated at room temperature, after acidification. It is highly probable that some silver chloride was lost at this stage. This accident emphasizes the importance of not overloading the aqua ammonia washings, rather than any serious weakness in the procedures. In fact, except for their "incidental" feature the new procedures were satisfactory in every respect, and under more favorable conditions, in "direct" gravimetric analyses, should be capable of even higher precision.

In conclusion, the significance of the present results as a determination of the atomic mass of sodium may be briefly noted. Seven of the titration analyses have been made with carefully purified reagents and materials, by a method in which it has not been possible to detect any constant errors greater than the known accidental errors of the analytical procedures. In deriving a value for the NaCl:Ag ratio from these seven experiments, convention requires the rejection of the abnormally high value, whereupon the remaining six give 0.541817 ± 0.0000010 for the ratio. Thus, if Cl = 35.457 and Ag = 107.880, the atomic mass of sodium is 22.994. Seven gravimetric analyses were made with sodium chloride containing no known impurities, but only five of these are properly eligible for use in estimating the NaCl: AgCl ratio. These five analyses yield the value 0.40779 ± 0.0000026, whence Na = 22.994.

Thanks are due to Professor George A. Hulett for many suggestions which have been found helpful in the present series of experiments.

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THE ACTIVITY COEFFICIENT OF THALLOUS CHLORIDE IN PROTEIN SYSTEMS[1]

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While the effect of salts upon the solubility of proteins has been studied by Mellanby (1), Sörensen (2), Cohn (3), Stadie (4), Florkin (5), Green (6), and others, the effect of proteins upon the solubility of salts has been little studied. Pauli and Stenzinger (7) have measured the solubility of calcium sulfate in various protein solutions. Failey (8) has studied the effect of edestin nitrate on the solubility of thallous chloride. These workers, however, have merely correlated the change in solubility of the salt with the protein concentration. In the present investigation this change has been related to the ionic strength of the solution as calculated under certain assumptions. Adair (9) determined the activity coefficients of chloride ion in edestin chloride solutions equilibrated with hydrochloric acid and correlated them with the charge on the protein in a manner similar to that developed in this paper.

PREPARATION OF MATERIALS

Egg albumin

This protein was prepared from the whites of strictly fresh eggs according to the method of Sörensen (2). The crystals obtained were dissolved and recrystallized three times from ammonium sulfate solution. The final material, placed in cellophane sacs, was dialyzed against running tap water for forty-eight hours, against distilled water for four days, and finally freed from electrolytes by means of electrodialysis. The approximately 5 per cent stock solution resulting left a negligible ash and was completely free of chlorides (see table 1). It had a pH of 4.75 and a conductivity of 7.6 × 10^{-5} mhos.

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[2] The material for this paper is from a dissertation submitted by Gilbert C. H. Stone to the Faculty of Pure Science, Columbia University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Edestin

Crystals of the protein were prepared by a modification of the Osborne method (10). Finely ground hemp seed was extracted with a 10 per cent sodium chloride solution. The resulting liquid, diluted with three times its volume of water at 50°C. and allowed to cool, deposited crystals of edestin. The protein was recrystallized five times from a 10 per cent sodium chloride solution and three times from a 7.5 per cent sodium nitrate solution by means of dilution. The resulting crystals were repeatedly suspended in water and centrifuged until free from electrolytes (see table 1). By placing the protein in water in a volumetric flask and adding a slight excess of 0.1 N sodium hydroxide a solution was obtained. The amount of alkali added was noted. The liquid was made up to volume and used as a stock solution.

TABLE 1

Analysis of protein preparations

SUBSTANCE	CHLORIDE ANALYSIS				ASH ANALYSIS
	N/10 hydrochloric acid added	Protein added (approximate)	Nitric acid added	Silver chloride obtained	Ash per gram of protein
	ml	*grams*	*ml.*	*grams*	*mg.*
	0.00	20	100	0.0002	
	20.00	0	0	0.2866	
	20.00	0	100	0.2867	
	20.00	0	100	0.2866	
Egg albumin	20.00	15	100	0.2866	2.19
	20.00	10	100	0.2865	2.71
Edestin	20.00	15	100	0.2868	0.0
	20.00	10	100	0.2867	0.1
Excelsin	20.00	15	100	0.2868	0.0
	20.00	10	100	0.2866	0.1
Hemoglobin	20.00	15	100	0.2864	5.42*
	20.00	10	100	0.2867	5.45*

* The amount of ash due to iron is given variously as 4.8–6.7 mg. per gram of hemoglobin.

Excelsin

This protein was also prepared by a modification of the Osborne method (11). The oil contained in a meal of finely ground Brazil nuts was expressed. The resulting solids were extracted with a 10 per cent sodium nitrate solution, and the protein recovered from this liquid by the addition of anhydrous sodium sulfate to 22 per cent by weight at a temperature of 37°C. According to Howe (12) this procedure completely precipitates globulins. The resulting precipitate was ground with 20 per cent sodium nitrate to dissolve it and the solution diluted with ten times its volume of water. A white amorphous precipitate settled out. The solid was three times dissolved in 20 per cent sodium nitrate and precipitated by dilution. The white amorphous material was finally dissolved in a minimum of 20 per cent sodium nitrate solution, placed in cellophane sacs, and dialyzed against running tap water for three days and against distilled water for three days. The precipitated globulin so obtained was pure white and crystalline. It was washed four times by suspending in water and centrifuging. From the electrolyte-free preparation (see table 1) a stock solution of the globulin was made up in the same manner as that of edestin.

Hemoglobin[3]

This conjugated protein was prepared according to the method of Stadie (13) by electrodialyzing fresh horse cells that had been previously washed four times in physiological saline solution. The crystals obtained, however, as noted also by Burk (14), even after washing with ice-cold distilled water, contained considerable quantities of salt, either bound or free. Therefore the crystals were dissolved in water and the cell debris removed by adding quantities of toluene and centrifuging—the stroma either becoming suspended in the toluene layer or settling to the bottom of the cup. The clear solution was once more electrodialyzed until salt-free (see table 1).

Reduced hemoglobin, used in these investigations, was obtained by evacuating the bottles containing the oxyhemoglobin, passing hydrogen through the solutions, and working with them in an atmosphere of hydrogen. Stock solutions had a pH of 6.75 and a conductivity of 4.8×10^{-5} mhos.

During the preparation of these proteins adequate amounts of c.p. toluene were added as a preservative. The proteins were used immediately after they were prepared, or stored, when necessary, in the ice-box under toluene.

To prepare electrolyte-free egg albumin and hemoglobin for the determination of their molecular weights by means of osmotic pressure measurements, Burk (14) used practically the same procedures as were described above. His values for the molecular weights agreed well with those ob-

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[3] The authors are indebted to Dr. B. Crieley of the Lederle Laboratories for kindly supplying them with fresh horse cells.

tained by means of other methods. This would indicate that electrodialysis of these protein solutions produced no deleterious effects.

Thallous chloride

The saturating salt was Kahlbaum's "zur Analyse" thallous chloride, recrystallized twice from distilled water and twice from conductivity water.

Sodium hydroxide

The 1.0 *N* alkali was made from a saturated chloride-free, carbon dioxide-free solution of Kahlbaum's sodium hydroxide from metallic sodium, by dilution with carbon dioxide-free water.

EXPERIMENTAL

The solubility of thallous chloride in water was determined as follows. Approximately 10 g. of saturating salt was suspended in 200 ml. of conductivity water in each of six glass-stoppered Pyrex bottles, and rotated for twenty-four hours in a water thermostat at a temperature of 25.00 ± 0.01°C. The salt was allowed to settle in the bottles in the thermostat and the saturated solutions filtered through cotton by means of a pressure syphon into glass-stoppered flasks. Samples of the solution were weighed out and chlorides determined gravimetrically as silver chloride.

An average of eighteen determinations involving three equilibrations gave the solubility of thallous chloride in water as 0.01612 ± 0.00003 moles per 1000 g. of water. This value checks with that of Bray and Winninghoff (15). In four of the determinations the solvent was saturated with toluene. No change in solubility resulted. The toluene with which the protein solutions were saturated, therefore, is a negligible factor.

In determining the solubility of thallous chloride in the protein solutions the same method of equilibrating and filtering was used, the solvent, however, being the protein solution. These solutions were made up by determining the per cent of protein in the stock solutions either by the Kjeldahl or the dry weight method. These gave concordant results. The nitrogen factors taken are as follows: Egg albumin 15.56 (16), edestin 18.69 (10), excelsin 18.30 (11), hemoglobin 16.86.

The solutions were then made up by weight from the stock solutions and the calculated amount of 1.0 *N* sodium hydroxide added.

A sample was removed for the determination of its pH.

The bottles containing the thallous chloride were washed three times with distilled water, then once with the appropriate protein solution before equilibrating.

The following procedure for determining chlorides in the protein solutions gave a maximum error of 0.3 per cent on solutions of known chloride content (see table 1). To weighed samples of the solution of approximately 100 g. a 50 per cent excess of silver nitrate dissolved in concentrated nitric acid was added. One hundred ml. of concentrated, chloride-free nitric acid was added to the solution and a few drops of caprylic alcohol to prevent foaming. The beakers were covered with watch glasses and digested overnight on a hot plate. The protein entirely destroyed by the nitric acid left the silver chloride coagulated and easily filterable. The solutions were allowed to cool to room temperature; the precipitate was washed thoroughly by decantation, filtered, and weighed.

TABLE 2

Effect of time on the solubility of thallous chloride in an excelsin solution at 25°C.

PROTEIN CONCENTRATION PER KILOGRAM OF WATER	TIME OF EQUILIBRATION	MOLALITY OF THALLOUS CHLORIDE
grams	*hours*	
35.52	24	0.01984
35.52	72	0.01985
35.52	120	0.01985
35.52	168	0.01985

TABLE 3

Activity coefficients of thallous chloride in isoelectric, electrolyte-free protein solutions

PROTEIN	CONCENTRATION OF PROTEIN IN GRAMS PER KILOGRAM OF WATER	MOLALITY OF THALLOUS CHLORIDE	$-\log \gamma \pm$ TlCl
Egg albumin	5.61	0.01622	0.0730
	11.13	0.01624	0.0736
	19.31	0.01640	0.0780
	29.63	0.01646	0.0793
	39.14	0.01647	0.0796
	47.49	0.01667	0.0850
Hemoglobin	10.79	0.01620	0.0724
	15.16	0.01631	0.0755
	22.77	0.01638	0.0773
	26.85	0.01648	0.0800
	31.03	0.01657	0.0824

The hydrogen-ion concentration of the solutions was determined at 25°C. by means of a Clark rocking electrode. Tenth normal hydrochloric acid was the reference standard, its pH being assumed to be 1.08. The hydrogen used was purified by passing it over copper at 650-700°C.

The densities of the solutions were measured by means of a Westphal balance at 25.0 ± 0.5°C.

In order to determine the time necessary for equilibrium to be attained

TABLE 4

Activity coefficients of thallous chloride in protein solutions of varying "ionic strengths"

PROTEIN	GRAMS OF PROTEIN PER KILOGRAM OF WATER	pH OF PROTEIN SOLUTIONS	C_{OH^-} OF SOLUTIONS $\times 10^3$	MOLALITY OF THALLOUS CHLORIDE	$-\log \gamma_t$	$\sqrt{\mu}$	$\sqrt{\mu_s}$
Egg albumin	1.228	12.25	25.00	0.01793	0.1168	0.230	0.275
	2.455	12.23	25.00	0.01808	0.1203	0.239	0.299
	4.910	12.19	25.00	0.01837	0.1272	0.246	0.317
	10.05	12.00	25.00	0.01959	0.1550	0.319	0.477
	20.11	11.76	25.00	0.02051	0.1750	0.333	0.511
	30.16	11.44	25.00	0.02064	0.1778	0.338	0.526
	40.22	11.02	25.00	0.02039	0.1724	0.329	0.511
	50.27	10.43	25.00	0.02002	0.1645	0.312	0.418
	20.00	5.03	1.00	0.01648	0.0799	0.131	0.132
	20.00	5.50	2.50	0.01663	0.0839	0.139	0.151
	20.00	6.34	5.00	0.01693	0.0917	0.162	0.201
	20.00	10.64	10.00	0.01805	0.1195	0.219	0.314
	20.00	11.78	25.00	0.02041	0.1729	0.331	0.507
	20.00	12.31	50.00	0.02204	0.2063	0.378	0.552
Edestin	5.001	12.22	25.00	0.01818	0.1226	0.229	0.497
	10.002	12.16	25.00	0.01855	0.1313	0.240	0.599
	20.00	12.01	25.00	0.01920	0.1464	0.264	0.786
	30.01	11.84	25.00	0.01957	0.1545	0.282	0.916
	40.01	11.62	25.00	0.01974	0.1584	0.290	0.980
	50.01	11.38	25.00	0.01954	0.1540	0.290	0.994
	4.536	12.80	100.00	0.02104	0.1860	0.316	0.490
	13.61	12.77	100.00	0.02163	0.1990	0.368	0.678
	24.95	12.72	100.00	0.02222	0.2098	0.403	1.018
	45.36	12.63	100.00	0.02353	0.2347	0.434	1.272
	20.00	11.21	10.00	0.01745	0.1047	0.202	0.595
	20.00	11.81	20.00	0.01861	0.1327	0.261	0.836
	20.00	12.11	30.00	0.01944	0.1517	0.286	0.877
	20.00	12.27	40.00	0.01993	0.1626	0.317	0.973
	20.00	12.40	50.00	0.02047	0.1741	0.331	0.962
Excelsin	3.058	12.24	25.00	0.01805	0.1195	0.223	0.439
	6.115	12.21	25.00	0.01812	0.1211	0.231	0.517
	9.173	12.16	25.00	0.01835	0.1266	0.243	0.622
	18.35	12.03	25.00	0.01902	0.1422	0.265	0.795
	36.69	11.62	25.00	0.01979	0.1594	0.298	1.023
	55.04	11.16	25.00	0.01952	0.1536	0.290	1.004
	20.00	10.43	5.00	0.01714	0.0971	0.160	0.133
	20.00	11.25	10.00	0.01730	0.1009	0.200	0.345
	20.00	11.84	20.00	0.01866	0.1340	0.254	0.627
	20.00	12.14	30.00	0.01922	0.1468	0.272	0.619
	20.00	12.30	40.00	0.01975	0.1587	0.297	0.704
	20.00	12.43	50.00	0.02013	0.1669	0.305	0.606

TABLE 4—*Concluded*

PROTEIN	GRAMS OF PROTEIN PER KILOGRAM OF WATER	pH OF PROTEIN SOLUTIONS	C_{OH^-} OF SOLUTIONS × 10^3	MOLALITY OF THALLOUS CHLORIDE	$-\log \gamma_\pm$	$\sqrt{\mu}$	$\sqrt{\mu_e}$
Hemoglobin	2.949	12.22	25.00	0.01777	0.1126	0.257	0.236
	5.529	12.12	25.00	0.01801	0.1185	0.314	0.273
	7.372	12.09	25.00	0.01771	0.1113	0.320	0.276
	10.30	12.01	25.00	0.01834	0.1264	0.331	0.686
	20.60	11.58	25.00	0.01943	0.1514	0.373	0.813
	30.90	11.10	25.00	0.02003	0.1648	0.360	0.781
	41.20	10.70	25.00	0.02014	0.1671	0.333	0.709
	51.50	10.35	25.00	0.02009	0.1660	0.310	0.646
	20.00	6.96	0.50	0.01647	0.0796	0.131	0.144
	20.00	6.84	0.10	0.01692	0.0915	0.130	0.135
	20.00	6.67	0.05	0.01651	0.0808	0.128	0.127
	20.00	7.28	1.00	0.01581	0.0618	0.128	0.133
	20.00	7.81	2.50	0.01602	0.0675	0.137	0.166
	20.00	8.65	5.00	0.01645	0.0792	0.160	0.246
	20.00	10.41	10.00	0.01752	0.1065	0.220	0.423
	20.00	11.52	25.00	0.01939	0.1506	0.252	0.461
	20.00	12.28	50.00	0.02005	0.1652	0.438	0.925

between the saturating salt and the solvent, and also to determine whether the solubility of the thallous chloride in the protein solutions varied with time owing to the action of the alkali on the protein, a time curve was made. Excelsin was dissolved in a solution of sodium hydroxide so that the alkali was 0.025 molal and the protein concentration 35.52 g. per 1000 g. of water. This solution was equilibrated in the usual manner with the thallous chloride crystals. Samples were removed and analyzed at the end of one, three, five, and seven days. The results are tabulated in table 2. It can be seen that the solubility of the thallous chloride is constant over the period of a week's equilibration, and that twenty-four hours of rotating the solution with the saturating salt is sufficient for equilibrium.

DISCUSSION

Tables 3 and 4 summarize the data and results of these experiments. The first table gives the negative logarithm of the activity coefficient of thallous chloride in the presence of isoelectric, electrolyte-free protein, calculated according to the equation (17)

$$-\log \gamma_\pm = \log \frac{1}{m^0_\pm} - \log \frac{1}{m_\pm} \qquad (1)$$

$\log \frac{1}{m^0_\pm}$ being taken as 1.8630 (18).

Figure 1 is a plot of the data in table 3 and some of that in table 4 with $-\log \gamma_{\pm}$ as ordinates and grams of protein per 1000 g. of water as abscissae. The lowest curve represents the effect of varying concentrations of isoelectric protein, without the addition of alkali, upon the negative logarithm of the activity coefficient of thallous chloride. The points fall on a straight line, the slope of which is quite small. Isoelectric, electrolyte-free protein, even in high concentrations, does not greatly effect the solubility of the saturating salt. If the decrease in the activity coefficient of the saturating salt be due to interionic effects, then isoelectric protein might be expected not to raise the solubility at all. However, at their isoelectric points proteins, on the basis of the zwitter ion theory, have a high total charge in spite of the fact that their net charge is zero—the number of positive and negative charges on the molecule being equal. In addition there probably exist a few molecules having a small net positive or negative charge which would be expected to cause a rise in the curve.

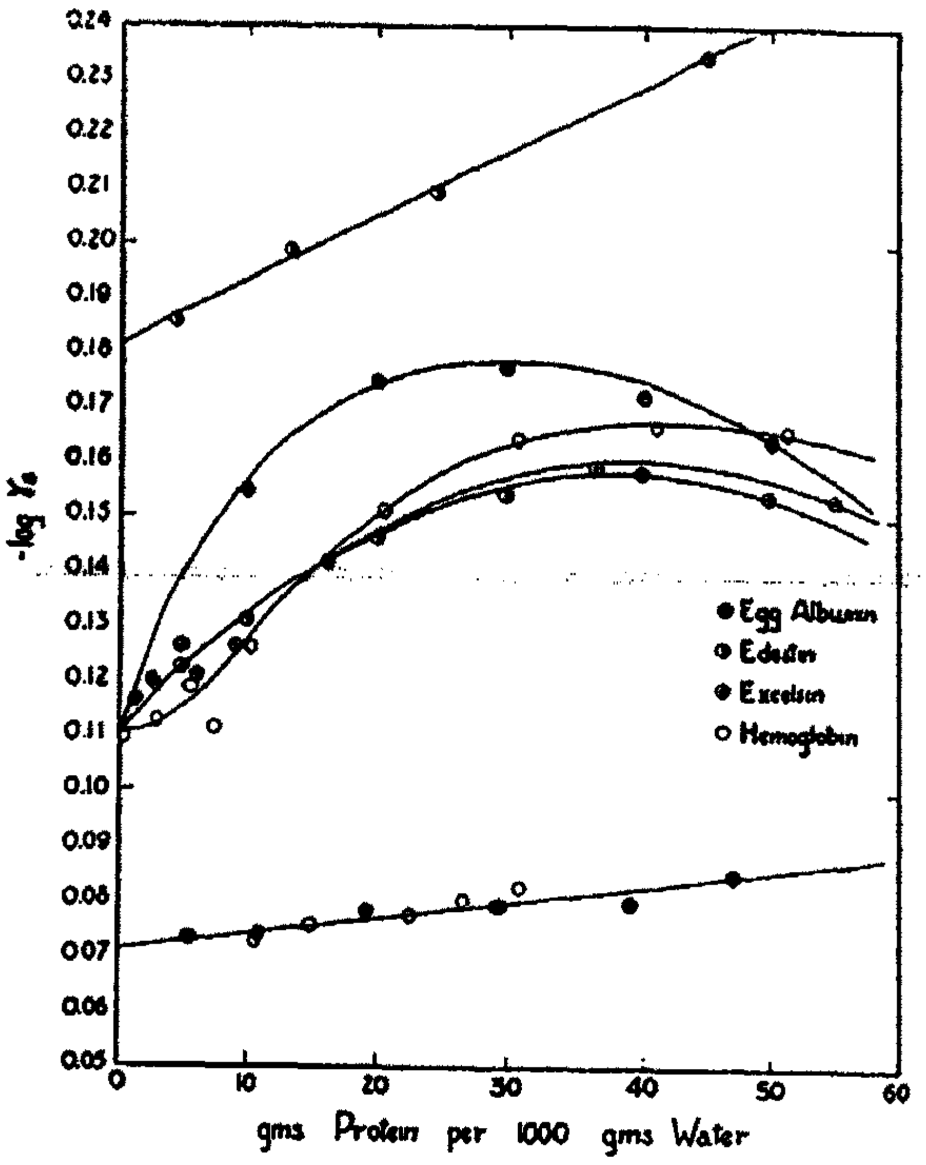

FIG. 1. EFFECT ON THE ACTIVITY COEFFICIENT OF THALLOUS CHLORIDE OF VARYING CONCENTRATIONS OF ISOELECTRIC, ELECTROLYTE-FREE PROTEIN SOLUTIONS, OF PROTEIN SOLUTIONS IN 0.025 *N* SODIUM HYDROXIDE, AND OF PROTEIN SOLUTIONS IN 0.1 *N* SODIUM HYDROXIDE

If base is added to an isoelectric protein solution, the molecules of the ampholyte acquire a net negative charge. Their effect on the activity coefficient of an ion may now be a function not only of the protein concentration but also of the charge on each individual protein molecule. As a first assumption one might expect the charged protein molecules to affect the activity coefficient of electrolytes as if they were contributing to the ionic strength an amount equal to the product of the square of their valence by their molality. Then in dilute solutions one should find, according to Debye (19),

$$- \log \gamma_{\pm} = 0.505 \sqrt{\mu} \qquad (2)$$

The number of hydroxyl ions bound in a protein solution is obtainable from pH measurements. The protein concentration being known, the protein molality and its contribution to the "ionic strength" may be calculated if a value be assumed for the molecular weight of the protein.

The points on the curve in the middle portion of the graph (figure 1) represent the effect of varying concentrations of protein in 0.025 N sodium hydroxide upon the negative logarithm of the activity coefficient of thallous chloride. It may be seen that the rise is at first linear with increasing protein concentration. Soon the curve slopes off and a maximum is reached after which $-\log \gamma_{\pm}$ falls with higher concentrations of ampholyte.

When high protein concentrations are employed, there is insufficient sodium hydroxide present to convert the molecules into their most basic sodium salt. These molecules, binding less base, do not raise the ionic strength of the solution as much as protein molecules at their maximum binding capacity. For this reason, as the protein concentration increases the ionic strength increases to a maximum. Then, beyond the point where it has combined with all the base present, the curve falls off. Further addition of protein serves to decrease the ionic strength. This phenomenon will again be noted when $-\log \gamma_{\pm}$ is plotted against $\sqrt{\mu}$.

In the case of hemoglobin, the curve does not rise linearly at first. This protein does not seem to behave like the others, as has been noted throughout the investigation. These abnormalities and the importance of hemoglobin biologically indicate that this protein merits further study.

The uppermost curve represents the effect of varying concentrations of edestin in 0.1 N sodium hydroxide upon $-\log \gamma_{\pm}$. Here a linear relationship exists, at least up to a protein concentration of 5 per cent. In this case there is sufficient alkali to satisfy the maximum binding capacity of the highest concentrations of edestin used. An increase of protein concentration in such alkaline solutions produces an increase in the ionic strength of the solution and a corresponding rise of $-\log \gamma_{\pm}$.

Figure 2 is a graph of the data in table 3, with $-\log \gamma_{\pm}$ as ordinates and $\sqrt{\mu}$, (on the basis of the molecular weights of the proteins as determined by Svedberg) as abscissae. Points were obtained for constant protein (2 per cent) and varying alkali concentrations, and also varying protein and constant amounts (0.025 N) of sodium hydroxide.

It will be noted that the points fall approximately on the straight dotted lines in the case of egg albumin, edestin, and excelsin. Hemoglobin seems to be at variance with this linear relationship.

However, according to equation 2 the slope of these lines should be 0.505, at least in the solutions of lowest ionic strength. A broken line of such slope is drawn on the graph. All the observed values fall below the theoretical. The ionic strengths were therefore recalculated, varying the apparent molecular weight, in order to obtain the theoretical slope. It was found that if an apparent molecular weight of 11,400 be assigned to each of the proteins, the ionic strength calculated on that basis would give points which lie on the same straight line having a slope of 0.505.

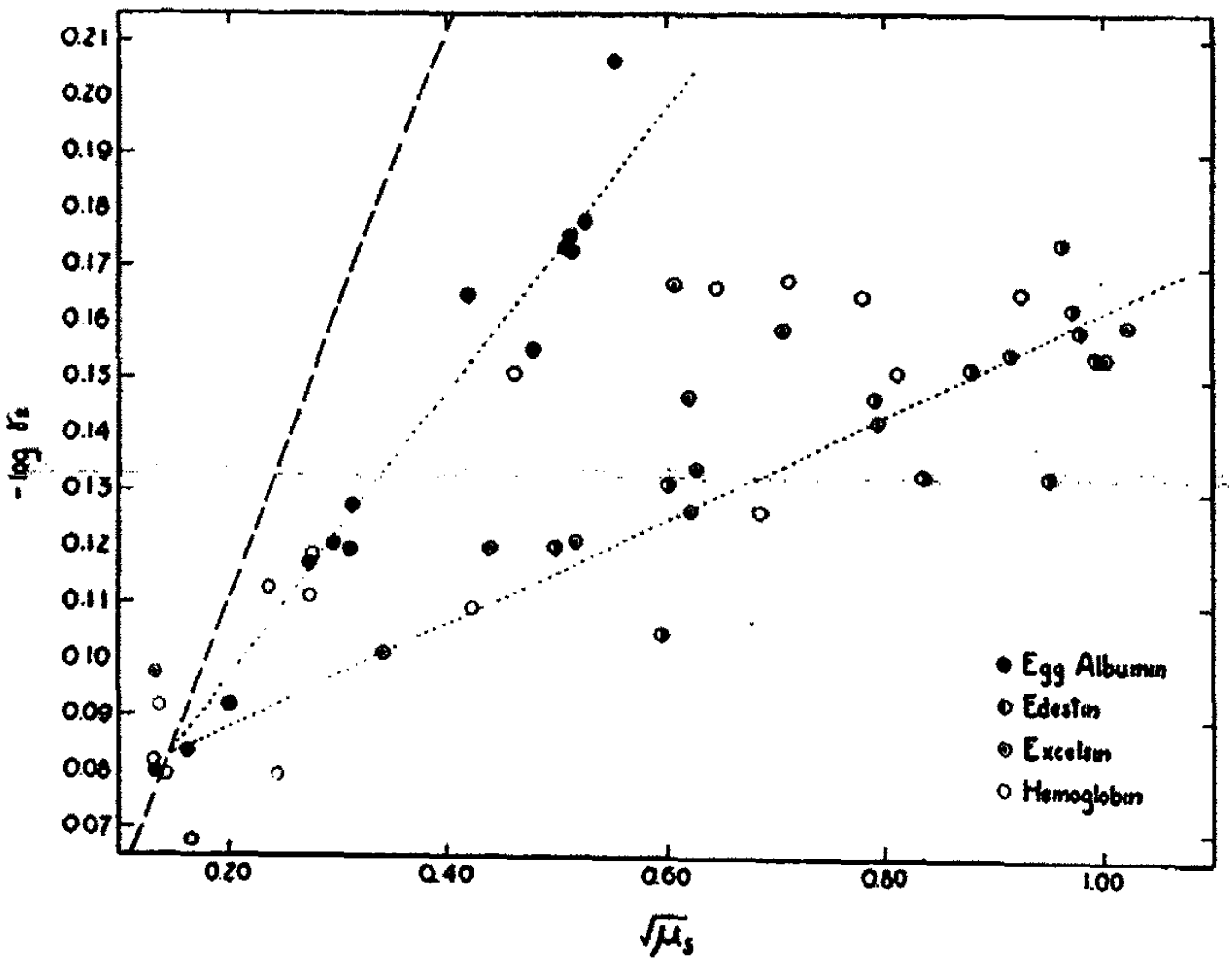

FIG. 2. INFLUENCE OF THE "IONIC STRENGTH" OF PROTEIN SOLUTIONS, CALCULATED ON THE BASIS OF SVEDBERG'S MOLECULAR WEIGHTS, ON THE ACTIVITY COEFFICIENT OF THALLOUS CHLORIDE

Table 4 gives these calculations and may require further explanation as to the method and theory involved. The molality has been computed by dividing the concentration of the protein, given in grams per 1000 g. of water, by the apparent molecular weight of 11,400. This value was assumed to be the same for all the proteins. Column 3 gives the pH as determined electrometrically. The concentration of hydroxyl ions was calculated from the pH on the basis that

$$aH^+ \times aOH^- = aH_2O = 10^{-14} \text{ at } 25°C. \qquad (3)$$

$$aH^+ \times [OH^-]\,\gamma_{OH^-} = 10^{-14} \qquad (4)$$

$$-\log [OH^-] = 14 - pH + \log \gamma_{OH^-} \qquad (5)$$

Since the activity coefficients of all uni-univalent electrolytes have approximately the same value at low ionic strengths, it was believed justifiable to assume γ_{OH^-} equal to $\gamma_{\pm TlCl}$.

Knowing the amount of hydroxyl ion added to the protein in the form of sodium hydroxide, and knowing the calculated value of the hydroxyl ion concentration of the solution after the addition of alkali, a simple subtraction gives the base bound by the protein. The apparent valence is the concentration of base bound divided by the molality of the protein, or the base bound per molecule of protein. These figures are not whole numbers, but rather an average valence. Owing to the complex structure of the proteins and the many dissociable hydrogen ions, at any instant not all the molecules may bear the same number of charges. It is rather the time average of the net charge that is important, giving an average valence.

TABLE 5

Densities of protein solutions at 25° C.

PER CENT PROTEIN	EGG ALBUMIN	EDESTIN	EXCELSIN	HEMOGLOBIN
0.5	0.9993	0.9992	0.9991	0.9992
1.0	1.0012	1.0012	1.0011	1.0012
1.5	1.0030	1.0030	1.0031	1.0030
2.0	1.0045	1.0048	1.0050	1.0046
2.5	1.0058	1.0064	1.0067	1.0060
3.0	1.0070	1.0079	1.0083	1.0073
3.5	1.0080	1.0092	1.0097	1.0084
4.0	1.0090	1.0105	1.0110	1.0094
4.5	1.0098	1.0117	1.0122	1.0103
5.0	1.0105	1.0128	1.0134	1.0112

From these data the "ionic strength" of the protein solutions may be calculated, which, when added to the ionic strength due to the residual sodium and hydroxyl ions and the dissolved thallous chloride, gives the total ionic strength of the solutions. This quantity changed from a weight to a volume basis by the aid of the table of densities (table 5) is given in column 7, since μ in equation 2 is calculated from molarities, not from molalities.

Values of $\sqrt{\mu}$, tabulated in column 8 were calculated in a precisely similar manner employing the particle size or molecular weights of Svedberg, measured by the ultracentrifuge method. Egg albumin was taken as 34,500 (20), hemoglobin as 68,000 (21), and edestin and excelsin as 212,000 (22, 23). It is these values that were used in the graph, figure 2.

In figure 3 the square roots of the ionic strengths as calculated in column 7 are plotted as abscissae and the values of $-\log \gamma_{\pm}$, column 6, as ordinates.

Egg albumin, excelsin, and edestin conform very well to the straight line curve of slope 0.505. The hemoglobin points, however, scatter around the line. Several different preparations were used. All showed the same effect.

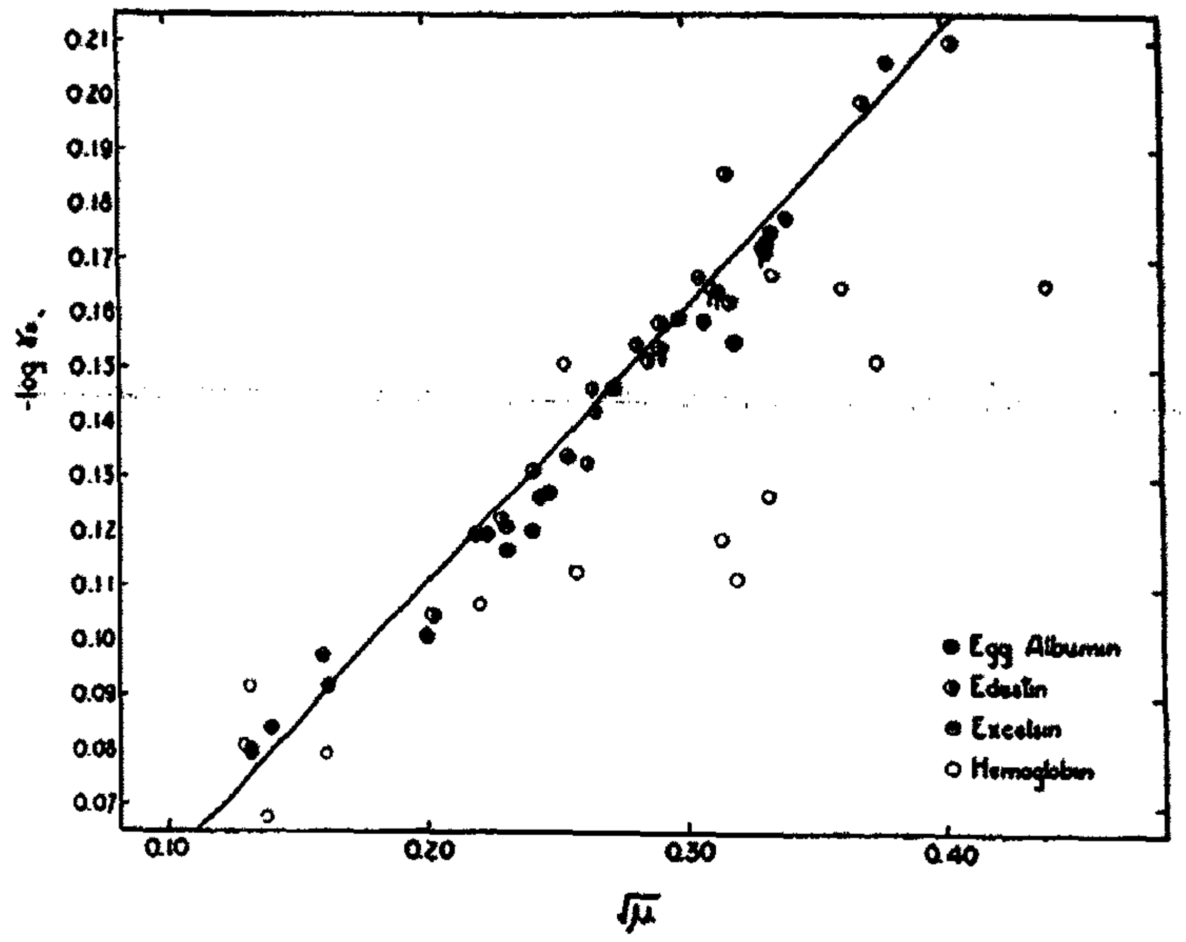

FIG. 3. INFLUENCE OF THE "IONIC STRENGTH" OF PROTEIN SOLUTIONS, CALCULATED ON THE BASIS OF AN ASSUMED MOLECULAR WEIGHT OF 11,400, ON THE ACTIVITY COEFFICIENT OF THALLOUS CHLORIDE

The points with arrows are those where the protein concentration is high; the ionic strength having reached a maximum the points have fallen back on the line below the maximum.

The fact that the negative logarithm of the activity coefficient is a linear function of the square root of the ionic strength calculated as above would indicate that sodium proteinates behave similarly to typical electrolytes. This is true even though the apparent valence of the protein be as high as 15, giving good accordance with the Debye limiting law up to ionic strengths as high as 0.18 when the molecular weight of 11,400 is assumed for each protein. However, this should be regarded as an interesting empirical generalization rather than as an indication that there really exist units of weight 11,400 and of high valence which behave in so simple a manner. The uniformity of action indicates an underlying similarity in the interaction between electrolytes and proteins of widely different character.

Perhaps the theory of polyvalent protein ions and their effect on the thermodynamic environment should consider the spacing of charges in addition to the net valence calculated on the basis of molecule size.

It must be noted that some solutions were quite alkaline—the pH rising from the isoelectric point as high as 12.5. At high pH values there might be a disaggregation of the protein into smaller units. Svedberg (23) noted this phenomenon while determining the molecular weights of edestin and excelsin. Near the isoelectric point the weight was 212,000 ± 4,000 but above the pH of 10.5 the molecules broke down into units having a weight of 34,500; he suggests that proteins are built up of these units (24). The "apparent molecular weight" found in the present investigation is 11,400, one-third of the unit 34,500.

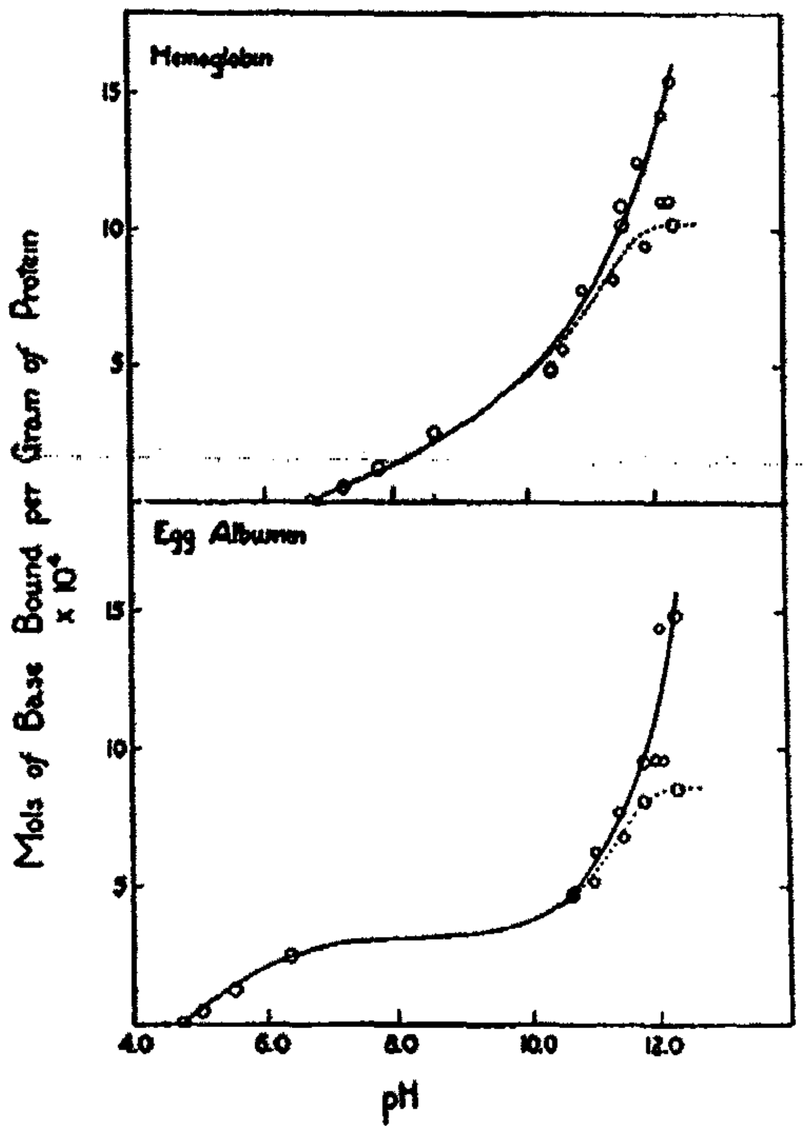

FIG. 4. CORRECTED AND UNCORRECTED TITRATION CURVES OF HEMOGLOBIN AND EGG ALBUMIN

In spite of the fact that the pH values cover a wide range over which, according to the above, a progressive disaggregation should occur, there is, except in the case of hemoglobin, no deviation from a linear relation between $-\log \gamma_{\pm}$ and $\sqrt{\mu}$ exceeding the experimental error.

Figure 4 is a plot of the titration curves of egg albumin and hemoglobin. The base bound per gram of protein is plotted as ordinates; the pH as abscissae. The data was taken from table 4.

When the base bound is calculated in the usual manner by subtracting the concentration of hydroxyl ions of the solution from the concentration added as sodium hydroxide, the $[OH^-]$ being obtained by the relationship,

$$-\log [OH^-] = 14 - pH \qquad (6)$$

the curves obtained are shown in solid lines and compare well with those found in the literature.

However, the concentration of hydroxyl ions must be corrected by means of the activity coefficient (equation 5). Then the base bound will at high pH values be found to differ considerably from that calculated by the first method. The titration curves obtained from such data are given on the graph by means of a dotted line. It can be seen that these corrected curves coincide with the uncorrected up to pH 10. At higher pH values the corrected curve falls lower to the extent of 20 per cent from the uncorrected. This correction factor of the activity coefficient is therefore necessary in order to obtain the true shape of a titration curve.

SUMMARY

1. The activity coefficient of thallous chloride in protein solutions was determined by means of solubility measurements.
2. In isoelectric, electrolyte-free protein solutions the change in solubility of the saturating salt was small, showing that such protein solutions exert little effect. The negative logarithm of the activity coefficient increased linearly with protein concentration.
3. The negative logarithm of the activity coefficient of thallous chloride was found not to be a linear function of the protein concentration in solutions of constant alkali content. A point of maximum solubility was obtained beyond which the solubility decreased in solutions of increasing protein concentration.
4. With solutions of varying protein content and constant alkali concentration, and varying alkali and constant protein concentrations, the negative logarithm of the activity coefficient of thallous chloride rose approximately linearly with increase in the square root of the ionic strength of the solution, calculated in accordance with certain assumptions.
5. If the apparent molecular weight of all the proteins be assumed to be 11,400, all points fell, except in the case of hemoglobin, on the same straight line of theoretical slope 0.505 when $-\log \gamma_{\pm}$ was plotted against $\sqrt{\mu}$.
6. A correction for titration curves was introduced.

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A CRITICAL STUDY OF SOME IRON-RICH IRON-SILICON ALLOYS

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On account of the technical importance of the iron-silicon alloys, considerable work has been done in recent years (1) on the constitution diagram of the system. Of particular importance both from the standpoint of the purity of the alloys used and the thoroughness of the investigation, is the work of Haughton and Becker, while the earlier work of Phragmen is also noteworthy. It appears that only the compound FeSi is accepted beyond dispute, while there is some doubt regarding the compounds Fe_3Si_2 and $FeSi_2$ (or Fe_2Si_5). The existence of a compound corresponding to Fe_3Si has been advanced by Corson; and Stoughton and Greiner, in their critical review of the literature and from their resistance study, also support Corson's view. On the other hand, Haughton and Becker, Phragmen, Murakami, and others deny the existence of Fe_3Si. Phragmen claims it to be merely a distinguished point in the series of solid solution, particularly because he found the limit of solubility to be 15.4 per cent silicon, as obtained, however, by extrapolation of the x-ray data.

In all the work done so far, each investigator appeared to be merely preoccupied with the interpretation of his results from a purely physical point of view, neglecting altogether considerations which would have been arrived at from a chemical standpoint. It is the writer's specific purpose to bring certain thermodynamic considerations to bear in the interpretation of his results as well as the results of other investigators. Hence, emphasis in this paper will be on chemical and not physical methods.

The writer has been particularly fortunate to have obtained through the kindness of Mr. K. Marsh of the Engineering Foundation Monograph Series, five samples of extremely pure iron-silicon alloys prepared in the Union Carbon and Carbide Research Laboratories, Inc. Some ordinary commercial iron-silicon alloys were also obtained from the Duriron Co., Dayton, Ohio. The composition of the alloys is given in table 1. It will be seen that the composition of the pure alloys in which the writer is mainly

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interested lies very close to that of Fe_3Si. The samples were received in the "as cast" condition and so they were annealed at about 900°C. for 150 hours in order to insure real equilibrium.

TABLE 1

Composition of the iron-silicon alloys

NO.	PER CENT Si	PER CENT Si BY ANALYSIS	NO.	PER CENT Si	PER CENT Si BY ANALYSIS
1	13.0	12.39	5	17.0	15.56
2	14.0	13.11	6*	5.0	4.92
3	14.5	13.99	7*	25.0	Not analyzed
4	15.0	14.50	8*	32.0	Not analyzed

* Commercial alloy.

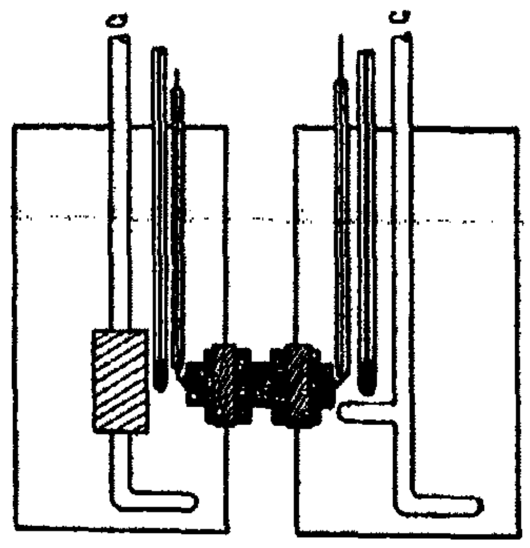

FIG. 1. APPARATUS FOR THE DETERMINATION OF THE THERMOELECTRIC CHARACTERISTICS OF IRON-SILICON ALLOYS

THERMOELECTRIC CHARACTERISTICS

Corson (1) made a study of the change in the resistivity of the iron-silicon alloys with respect to the silicon content, but on account of the fact that he used specimens which were not sufficiently annealed to obtain real equilibrium, doubt has been cast on this phase of his work. It is well known that the true value of the resistance of alloys is very difficult to measure except in the form of a wire, but from a study of Corson's paper the writer is convinced that no systematic error can account for the very sharp cusp at the composition corresponding to Fe_3Si.

As a general rule, the resistance curve is parallel, if not congruent, with the thermoelectric curve, and since the thermoelectric characteristics can be studied much more accurately, the writer adopted this method to ascertain if a similar cusp could be found. As the specimens were only 2 to 6 cm. in length and about 1.5 cm. in radius, a special but simple apparatus had to be constructed as shown in figure 1. The thermal E.M.F. was read against pure nickel at 75°C. and 50°C. at the hot junction and at 0°C. at the cold junction. After considerable trial, we found that by stirring the mushy mixture of pulverized ice in water at a speed of 1500 r.p.m., while the hot water was stirred at a speed of only 500 r.p.m., strictly reproducible results could be obtained. The millivoltmeter used was calibrated against a standard cell on the Type K (Leeds and Northrup) potentiometer. The results of this study are shown in figure 2.

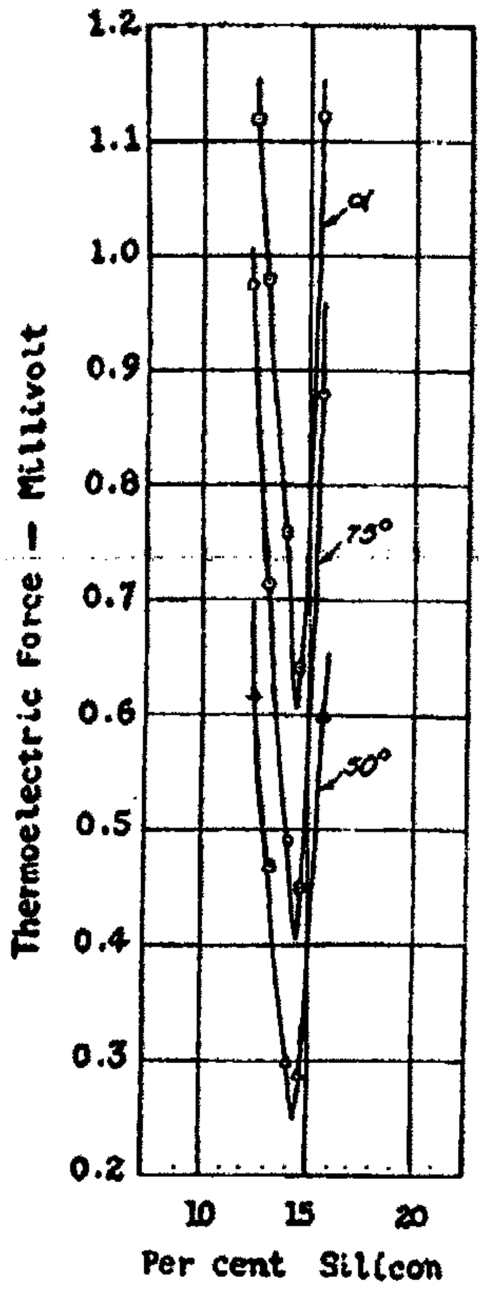

FIG. 2. THE THERMOELECTRIC CHARACTERISTICS OF SOME IRON-SILICON ALLOYS AGAINST NICKEL

The temperature coefficient (α) is also given

The sharp cusp in the resistivity-composition curve obtained by Corson is thus confirmed in figure 2, and since the composition of the alloys used by the writer varied by only small increments, the cusp may be placed with some certainty at exactly 14.35 per cent silicon, corresponding to the compound Fe_3Si. As Corson properly pointed out, the resistivity-composition curve he obtained is characteristic of a binary system of two metallic components forming a continuous series of solid solutions, either or both of which components may also be a truly intermetallic compound. Hence, if the alloy corresponding to the composition of 3Fe/Si were only a distinguished solid solution, the resistivity-composition curve should reasonably be expected merely to vary continuously from the resistivity of pure iron to that of 3Fe/Si without passing through a maximum, as was obtained by Corson. If we consider a truly metallic compound as one that is characterized by low resistivity, then Fe_3Si (hereafter designated as ϕ for convenience) is a metallic compound of the shared electron type, i.e., a nonpolar compound.

THE ELECTRODE POTENTIAL OF IRON–SILICON ALLOYS

The electrode potentials of alloys are very significant characteristics of their condition in the heterogeneous systems, i.e., whether compounds or solid solutions are formed. Suppose we have a cell with pure iron as one electrode and an iron–silicon alloy as the other electrode, both being immersed in the same solution of electrolyte (such as ferrous sulfate); then when a current passes through the cell, a certain quantity of iron is transferred from the pure iron electrode to the alloy electrode, thus

$$\text{Fe(pure)} = \text{Fe(in solid solution)};\ \Delta F = RT \ln a' = -\mathbf{N}\mathbf{E}\mathbf{F}$$

Hence,

$$\mathbf{E} = -(RT/\mathbf{NF}) \ln a' = -k \ln a' \qquad (1)$$

when the activity of pure iron is taken as unity and a' represents the activity of iron in the solid solution. It is noteworthy that the electrode potential in equation 1 is independent of the nature and concentration of the electrolyte used, provided **N** is the same.

In the case of an intermetallic compound acting as an electrode, the problem becomes much more complicated, as we no longer have an essentially ionic transfer following the Faraday law of electrolysis. This is due to the fact that intermetallic compounds, as a rule, are not of the polar type. The electrode potentials thus obtained may be meaningless, in regard to their thermodynamic significance, being perhaps nothing better than the polarization potentials. Nevertheless, even the polarization potential is also characteristic of the compound and that compound alone, and is, therefore, significant in revealing the presence of a particular compound.

In figure 3 is shown the experimental set-up for the determination of the electrode potential of the iron-silicon alloys against pure iron. The electrolytic hydrogen was first purified in a pyrogallic acid train, then in a platinized asbestos train, heated to about 500°C., and then bubbled through the boiling distilled water in the flask A, the stirring helping to rid the water of any dissolved gases on account of their mutual solubility (i.e., providing a gas-gas interface). After the water had been boiled for thirty to forty-five minutes, a cooling vessel was introduced under the flask. When the water had reached room temperature, the measuring bulb B was evacuated by a pump, and water was allowed to flow in from the reservoir flask A. This operation was repeated, so that the second time we were more certain that the bulb B contained only gas-free water. The requisite amount of the $FeSO_4 \cdot 7H_2O$ salt to make a $N/10$ solution was placed in the cell chamber C and the electrodes introduced as shown in figure 3. The cell chamber was then evacuated and hydrogen allowed to flow in. Stopcocks Nos. 2 and 3 were then opened, so that the flowing hydrogen could force the water from the measuring bulb B into the cell chamber C. During the course of the run, hydrogen was bubbled through the solution at the rate of a bubble per second. The potential was measured on a Type K potentiometer.

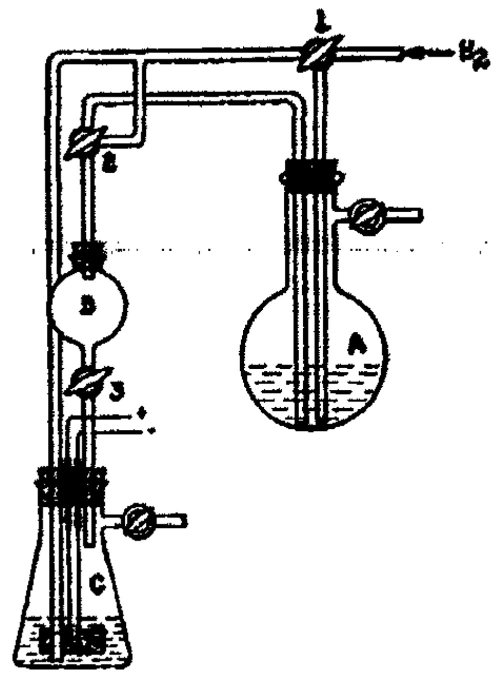

FIG. 3. APPARATUS FOR THE DETERMINATION OF THE ELECTRODE POTENTIAL OF IRON-SILICON ALLOYS AGAINST PURE IRON

The electrolytic iron electrode was kindly prepared for the writer by Mr. T. S. Fuller of the General Electric Research Laboratory. It had been previously remelted twice under very high vacuum. The ends of the electrodes were polished in the same manner as for metallographic examination. It was found that without proper etching, the cell did not come to equilibrium for as long as two weeks. After many trials, it was finally decided to use the ordinary $HF-HNO_3$-glycerine etchant as well as aqua regia. The latter drastic treatment was found necessary in order to remove the effect of cold-working during the process of polishing. In order to remove any surface inequalities due to preferential dissolution, all alloys were again repolished lightly and etched with a weaker solution of $HF-HNO_3$-glycerine. The electrodes, with the exception of the polished surface, were given a smooth coating of paraffin.

A few words may be said regarding the process of recrystallization of the $FeSO_4 \cdot 7H_2O$ salt, as it is very difficult to keep in a reduced state. In the preliminary part of the work, considerable trouble with oxidation of the ferrous salt solution was encountered, but when the recrystallized salt was later used, the trouble disappeared altogether. Baker's ordinary C. P. brand of the salt was dissolved in freshly distilled water to form a saturated solution. Then 95 per cent alcohol saturated with paraffin was added to precipitate the hydrate, $FeSO_4 \cdot 7H_2O$.[2] The salt was collected and allowed to dry on porous porcelain and then kept in a bottle covered with black paper. In this way, on account of the adsorption of the paraffin on the surface of the salt, the ferrous salt was well protected from oxidation for a long time.

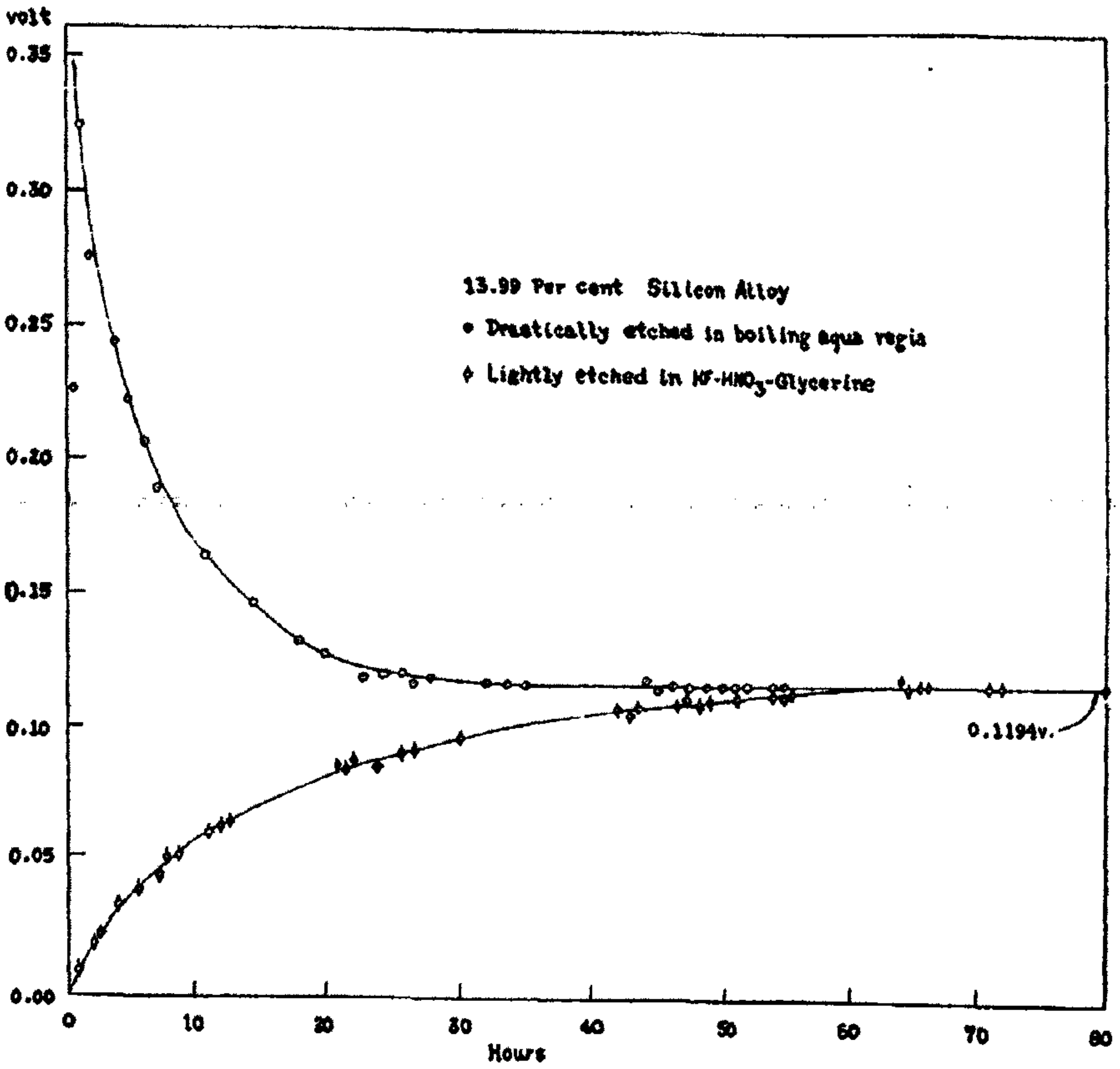

FIG. 4. THE CHANGE IN THE ELECTRODE POTENTIAL OF AN IRON-IRON-SILICON ALLOY WITH RESPECT TO TIME

Note that the equilibrium is approached from both sides.

[2] The salt was merely assumed to be the heptahydrate; no actual analysis was made.

In figure 4 is shown a typical example of how an iron–silicon electrode comes to an equilibrium in the cell. The upper curve is that due to the alloy electrode that was etched in boiling aqua regia, while the lower curve is that due to the alloy that was etched less drastically with the HF–HNO_3–glycerine etchant. While the upper curve suggests polarization phenomena, the lower curve proves that this is not the case. The fact that equilibrium is approached from both sides indicates that the cell is apparently reversible. In the absence of other pertinent thermal data (e.g., entropy, heat of formation, etc.), we are unable at present to interpret the actual significance of the electrode potential, although the activity of iron can be directly calculated from equation 1. In the range up to 5 per cent silicon (by weight) the electrode potentials are very small, so that the influence of impurities and surface conditions becomes marked; no attempt was therefore made to measure E nor dE/d*T*.

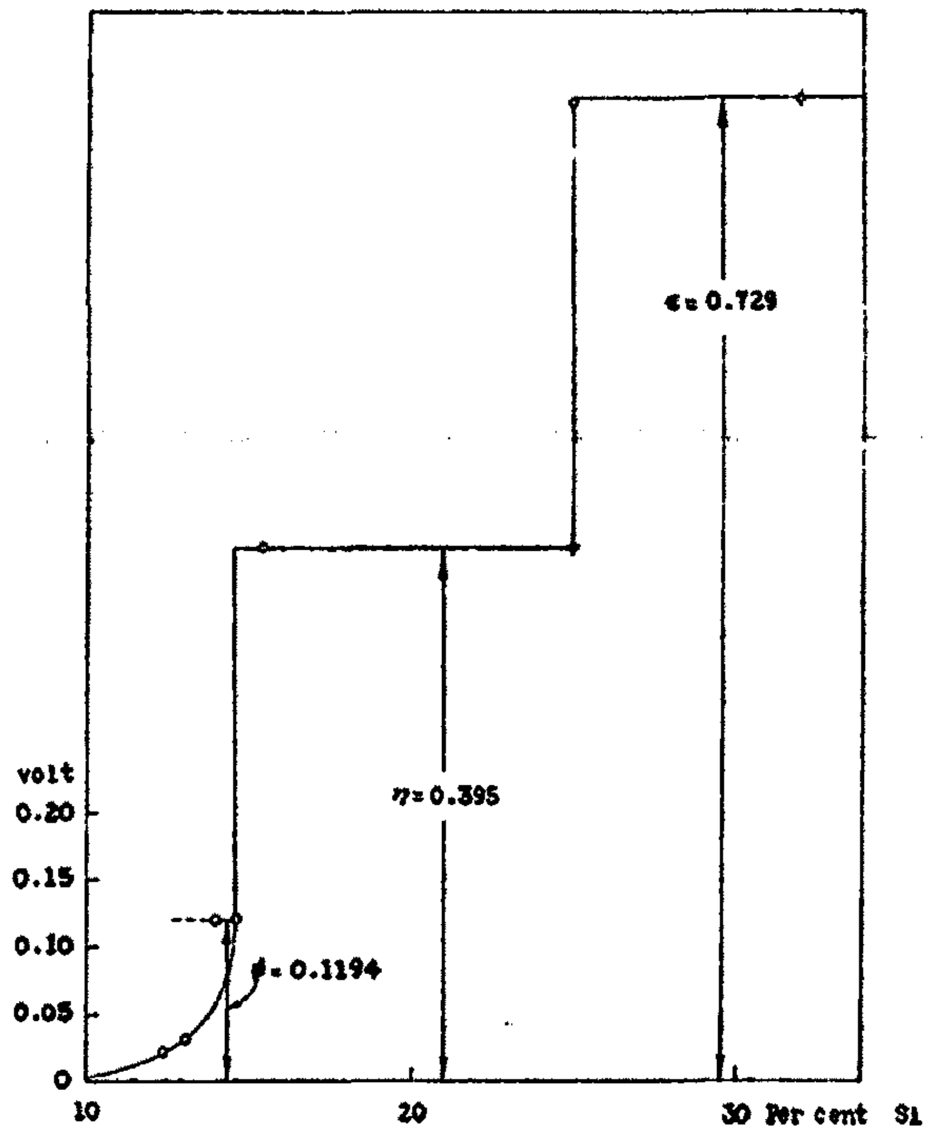

FIG. 5. THE ELECTRODE POTENTIAL OF SOME IRON–SILICON ALLOYS

Although theoretically the electrode potential of the 13.99 per cent silicon alloy should be much less than that of the compound ϕ, the observed potential is, however, that of the compound as shown in figure 5. This may be attributable to the fact that after long annealing at high temperatures, there must have been some tendency (present in all solid solutions) towards unmixing of the components in solution—in this case, apparently to iron and ϕ. If the solute were silicon, we would hardly have obtained the potential characteristic of ϕ. This suggests that the electrode potential method of determining the phase structure in an alloy is very sensitive. The existence of a compound Fe_3Si_2 (η) is also confirmed. That the compound is a result of a peritectoid reaction "$\phi + \epsilon \rightleftharpoons \eta$" is shown in a very interesting way as follows: a commercial 25 per cent silicon alloy showed a potential of about 0.725 volts in the "as cast" condition, indicating the presence of ϵ, but another sample in the annealed condition showed a potential of about 0.395 volts, which is the potential characteristic of η. It also appears from this observation that η does not form solid solutions with other impurities found in the commerical alloys and that the composition appears to be constant. The electrode potential of ϵ is about 0.725 to 0.729 volts, considerably higher than that of η.

MICROSCOPIC EXAMINATION OF THE ALLOYS

For the purpose of correlating the results, a microscopic examination of the alloys was made. It is quite true, as Corson pointed out, that no metallographic evidence has ever been produced proving conclusively the existence of the compound η. In the hope that the compound η might not belong to the isometric system, the writer used a polarizing microscope (Reichert make) in an attempt to detect its presence in the 15.56 per cent silicon alloy, but no positive confirmation could be obtained. In the case of the 13.99 per cent silicon alloy, the electrode potential indicates the presence of some ϕ and so the alloy was studied intensively to ascertain if ϕ can be distinguished from the ordinary solid solution. An attempt to study the inner symmetry of ϕ by means of etch figures failed, because even boiling aqua regia did not yield etch figures. The specimen was then placed in a ferrous sulfate solution and allowed to oxidize in the air for about one month. This resulted in the production of some etch figures (square and rectangular pits), but they were located in places where their position could not be correlated with respect to the large grains.[3] It should be noted here, however, that the microscopic evidence presented by Corson regarding the existence of ϕ is highly questionable in value. The "bushings" he observed were probably due to strains produced either in the process of cooling from the melt or during the polishing operation of the metallographic samples.

[3] It was hoped that if segregation of ϕ had appreciably taken place within a large grain, the etch figures in one part of the grain might differ in orientation and shape from those in other parts of the grain where ϕ is localized. The only indirect evidence of ϕ in the sample lies in the fact that certain grains (rather small and located within a large grain) were apparently unattacked by any chemical reagent, however drastic the treatment.

X-RAY ANALYSIS OF THE ALLOYS

Although Phragmen had made a careful x-ray analysis of the iron-silicon alloys he prepared, he did not use as pure alloys as the present writer has under investigation. The alloys, although already annealed for 150 hours at 900°C., were given another 150 hour annealing at the same temperature and cooled down to room temperature in 24 hours in order to determine whether a hyperstructure might be formed in the alloys with less than 14.35 per cent silicon, as a result of further unmixing of the components in solid solution.

Although the accuracy of the x-ray measurements on films taken with the ordinary cassettes that come with the General Electric Co. apparatus is only of the order of ±0.005Å., the absolute error can be minimized as follows: If we use as a standard for comparison pure iron, whose lattice parameter is known accurately, then as the effect of silicon is merely to shift the diffraction lines, the absolute length of any diffraction line from zero beam can be calibrated each time against the known (calculated) length of the corresponding line for pure iron. In this way, irrespective of the shrinkage of the film (which is about 12 in. long) or slight inaccuracies of the cassettes used, the absolute error is thus reduced to about ±0.001Å. As a result of several sets of measurements, the lattice parameter of the electrolytic iron used by the writer was determined to be 2.860Å. The films were measured on a small "home-made" comparator accurate to about 0.002 cm.

The results of the present investigation are graphically shown in figure 6 in comparison with those obtained by Phragmen. According to him, an alloy of the composition 3Fe/Si is merely a distinguished point in a series of solid solutions. The fact, however, that the lattice parameter of ϕ obtained by the writer is the same as that found by Phragmen, while in the range of solid solutions appreciable differences occur, is cogent argument in support of the assumption that ϕ is a compound. According to figure 6, the limit of solid solution is exactly that represented by ϕ. The difference in our results may be explained as follows: As unmixing takes place, the solid solution decreases in concentration with respect to silicon, hence, the fundamental lattice constant of the solid solution should increase accordingly.[4] We should, therefore, expect the diffraction lines of both the solid solution and ϕ to be present, but this was not the case. It should be

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[4] Since this work was completed, the writer has been able to increase greatly the accuracy of the G. E. cassette by a special device, on which a patent is being obtained. The pure alloys were unfortunately spoiled in the course of some other experiments. However, the 5 per cent silicon commercial alloy was again analyzed and was found to have a lattice constant of 2.856_7 Å. based on pure sodium chloride.

pointed out that the x-ray method is rather insensitive for the detection of small amounts of a second phase.

With the composition represented by 3Fe/Si, it appears reasonable to assume with Phragmen that if we take twice the size of the unit cell of iron and distribute the silicon atoms at the corners and face-centered positions, we have what corresponds to the hyperstructure of ϕ, with a fundamental lattice constant of 5.630Å. On a film taken with a rotating Debye-Scherrer type of camera, the only additional line determined with some certainty was 311, although even mere faint traces were also found which could be ascribed to the 2 (100) and 2 (111) planes. Although this is thus a confirmation of the regular distribution suggested by Phragmen, the x-ray method cannot by itself determine whether ϕ is a solid solution or a compound, as it does not describe the force-field between the different atoms in the lattice.

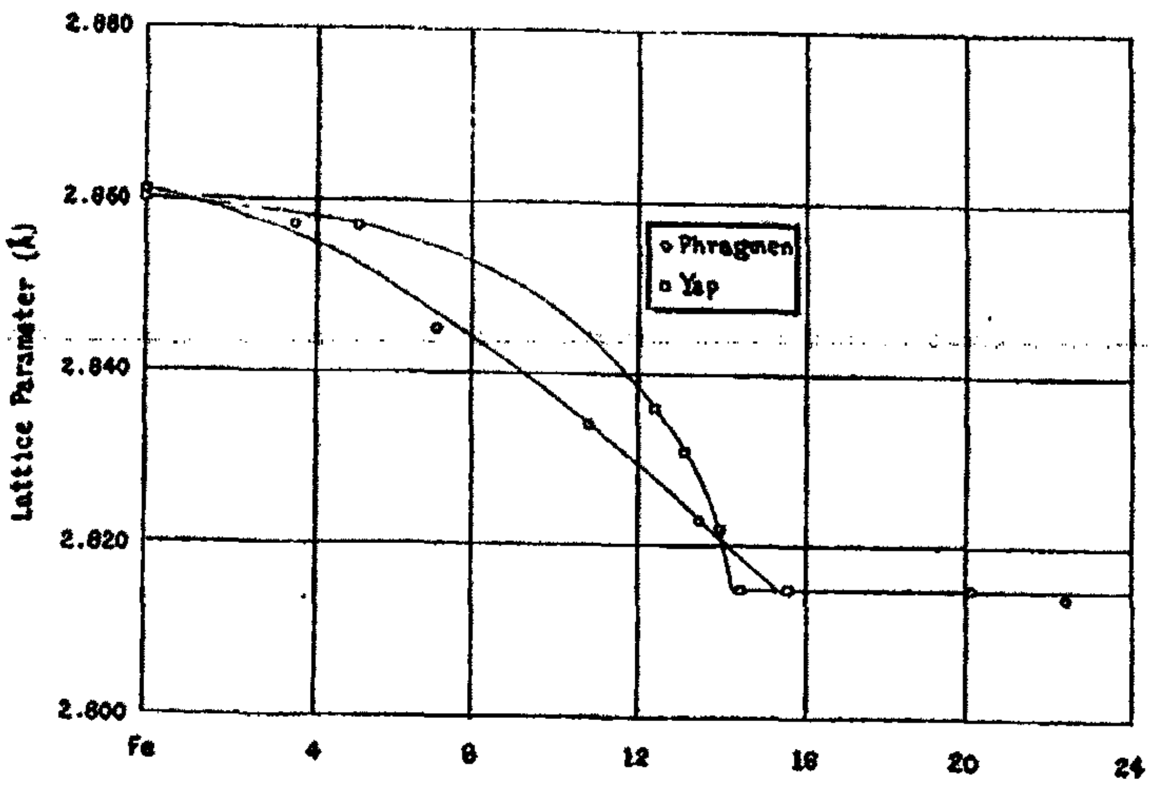

FIG. 6. THE CHANGE IN THE SIZE OF THE UNIT CELL WITH RESPECT TO SILICON CONTENT

THERMODYNAMIC CONSIDERATIONS OF THE EQUILIBRIA

A critical study of the original papers by Tammann, Kurnakow, Gontermann, Sanfourche, *et al.*, reveals that their results can be consistently interpreted as showing a "singular point" in the liquidus–solidus curves at about 14.4 per cent silicon, although according to Haughton and Becker, the singular point is about 12.2 per cent silicon. If the singular point were at 14.35 per cent, then the phase diagram of the iron–silicon system could be easily represented as a composite of the following binary systems: Fe–Fe_3Si, Fe_3Si–FeSi, FeSi–$FeSi_2$, and $FeSi_2$–Si. In such a case, the phase rule itself justifies us, even in the absence of any kind of independent evidence, in treating Fe_3Si as a compound.

It can be shown from thermodynamics that in heterogeneous equilibria involving the melt and a solid that is a solid solution (2)

$$\frac{d \ln(a/a')_A}{d(1/T)} = \frac{\Delta H_A}{R} \tag{2}$$

in which a is the activity of A in the melt and a' its activity in the solid solution. When we substitute mole-fractions for activities, equation 2 reduces to

$$\frac{d \ln(N'/N)_A}{d(1/T)} = \frac{\Delta H_A}{R} \tag{3}$$

so that if we plot ln (N'/N) against $1/T$, the slope of the curve as $(N'/N) \doteq 1$ should give us the correct value of ΔH_A, the heat of fusion of the pure solvent at its melting point. We are here required to make some *a priori* assumption regarding the nature of the solute, when the solvent alone is a pure and simple substance, like iron. In figure 7, curve I is calculated on the assumption that the solute is in the form of silicon atoms. We know from thermodynamic considerations that a positive deviation from Raoult's law is normally associated with an absorption of heat and an expansion in volume, and a negative deviation is accompanied with the opposite effects; the former also indicates a tendency towards unmixing, while the latter indicates a tendency towards the formation of compounds (3). As ideal solutions are defined from the standpoint of Raoult's law, any deviation from Raoult's law will be indicated by the deviation from the ideal solubility curve.[5]

We note that curve I shows a large negative deviation, which thus indicates that the solute forms a compound with the solvent atoms. Hence, curve II is calculated on the assumption that the solute is Fe_3Si, which is also evidently incorrect, as it gives 108.5 calories per gram as the heat of fusion of pure iron. We note, however, that curve II is linear for some range of temperature and concentration, and this constant deviation indicates a definite change in the ratio of molar concentrations, or, what is equivalent to it, a change in the total moles taking part in the equilibria. If we thus assume the solute to be $(Fe_3Si)_2$,[6] then we obtain curve III, which

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[5] In a strict sense, when solid solutions are involved in the equilibrium with the melt, the term "ideal solubility curve" is meaningless, as each solute will have a characteristic distribution constant.

[6] It is indeed curious—perhaps entirely accidental—that all compounds in the iron-silicon system can be represented by Fe_6Si_n, where *n is an even number*. It may be recalled that silicon, like GeGe, GeAs, ZnSe, ZnS and CC (diamond) is of the covalent type and may be considered diatomic. In view of this fact, the assignment of the formula $(Fe_3Si)_2$ or Fe_6Si_2 becomes reasonable.

gives the correct heat of fusion of iron, 65 calories per gram as the curve approaches the concentration pure iron, that is, as (N′/N) ≐ 1.

Just what is the real significance of polymerized molecules of $(Fe_3Si)_2$ existing in the melt and in solid solution, the writer is unable to say at present; neither is he interested in building up a mechanistic picture of such a compound. In the final analysis, provided the determination of the liquidus and solidus curve is sufficiently accurate and the heat of fusion of the solvent metal is known, the constitution of the solute in solution is revealed with some certainty by the thermodynamic laws relating to the depression of the freezing point. There are, of course, other sources of evidence of the reality of the existence of molecular solutes in the liquid state (e.g., studies in magnetic susceptibility, resistance, specific volume, Raman spectra, etc.), although the existence of the molecular solute in solid solution is much more difficult to prove. Given a saturated metallic solid solution in equilibrium with some excess solid solute in the form of an intermetallic compound AB; the common conception is that AB is dissociated to A + B upon dissolution in the solid solution. It is difficult to conceive, from strictly thermodynamic considerations, of the solute molecules magically dissociated in solution and yet in equilibrium with the solid solute (AB) whose dissociation pressure may be extremely small. I have already pointed out elsewhere (4) that if this were true, it should then be easy enough to construct a perpetual machine by simply lowering and elevating the temperature of a saturated solid solution.

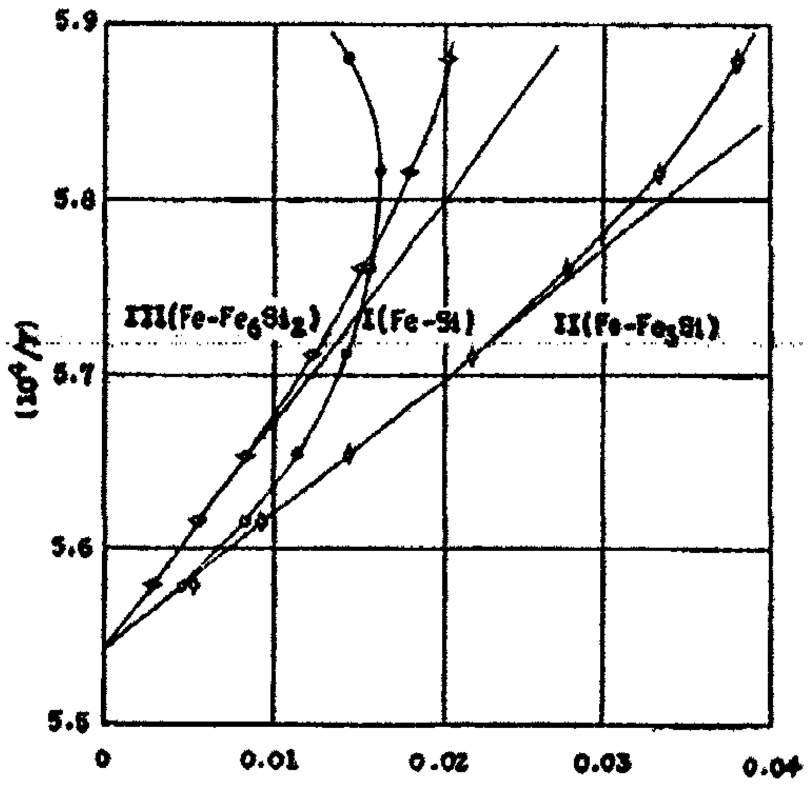

FIG. 7. THE LOG (N′/N).T^{-1} CURVES PLOTTED ACCORDING TO EQUATION 3

In order to ascertain if the degree of error in the thermal analysis can adequately account for the displacement of curve II in figure 7 from the ideal position, backward calculations were made on the assumption that the solidus is correct, as it was determined by Haughton and Becker by the Heycock-Neville method.[7] The calculated error in the location of the liquidus appears too large to be accounted for in this manner. The effect of silicon vapor on the reproducibility of a thermocouple is well-known and the accuracy of the thermal analysis of the primary solidification range may not be any better than ±5°C. On this assumption, the liquidus and solidus curves drawn by Haughton and Becker have been redrawn as shown in figure 8, in which $(Fe_3Si)_2$ is shown to have a definite melting point at 1250°C.

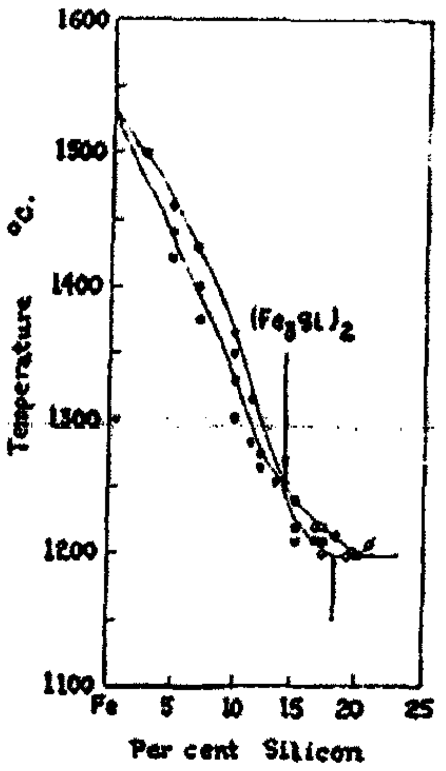

FIG. 8. THE PRIMARY SOLIDIFICATION RANGE OF IRON-SILICON ALLOYS (AFTER HAUGHTON AND BECKER)

STABILITY OF SOLID SOLUTIONS

Some remarks regarding liquation (i.e., unmixing) and consequent segregation of the components in solid solution may not be amiss in this paper. Let us conceive of a metallic system, A and B, which forms a complete series of solid solutions and in which no compounds are formed in the melt. The free energy of the system is at a minimum when A and B are distributed in such a manner that any unit portion (say a unit cell) has the same free energy content as any other unit portion. It is obvious that in a cubic system this condition is attained in the solid state only when the atomic fraction is a multiple of 1/8 when the solute atoms can be assigned a definite

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[7] The Heycock-Neville method involves quenching alloy specimens to successively higher temperatures and then examining the structure microscopically. The structure will be quite characteristic when the solidus temperature is reached.

position in the space lattice. This is the basis of Tammann's conception of regular distribution as "limits of resistance," as opposed to Vegard's view of the atoms being statistically (irregularly) distributed. In the liquid state where the atomic (and molecular) mobilities are much higher than in the solid state, a statistical distribution satisfies our conception of a homogeneous system, characterized by the lowest free energy; on the other hand, a solid solution may be expected to approach true homogeneity only as it approaches some form of regular distribution. When a solid solution is truly homogeneous, its free energy per mole (or gram-atom) is given by the equation

$$F = N_1\bar{F}_1 + N_2\bar{F}_2 = RT(N_1 \ln a_1 + N_2 \ln a_2) \qquad (4)$$

where $\bar{F}_1$ and $\bar{F}_2$ are the partial molal free energies of transfer of A and B (indicated for convenience by subscripts 1 and 2, respectively) from the pure state to a solid solution of activities a_1 and a_2, respectively. When the system obeys the laws of ideal solution, then $a_1 = N_1$ and $a_2 = N_2$ and their respective activities will vary linearly from 1 to 0 as shown in figure 9. The activity–composition curves (1′) and (2′) indicate a negative deviation, hence a tendency towards compound formation.

If the activity–composition curves were something like those shown in figure 10, all solid solutions between the composition of X and Y will have a tendency towards unmixing, whilst between A and X and between Y and B, a strong tendency towards compound formation exists (5). The problem then arises as to which of these two opposing tendencies is the more dominant and under what conditions one is more likely to occur than the other. From strictly graphical analysis of the phase diagram, when the solidification range of the solid solutions is wide, we may reasonably anticipate the system to show a tendency to liquate.[8] When the liquidus and solidus curves are very close together, then the solid solutions will melt over such a small temperature range as to behave as a unary substance, i.e., as a compound in this case. It should be noted, however, from phase-rule considerations, that as long as we have a solid solution, there will be a temperature range of melting, however small.

The problem now arises as to whether or not a regular distribution is a compound. According to our strict interpretation of homogeneity (based on the elementary cell as a unit) a regular distribution merely represents an extreme form of an ideally homogeneous distribution in the solid state, but it is also self-evident that we are stretching the criterion of homogeneity

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[8] This fact will become more evident when we recall that the phase diagram of two substances completely immiscible in each other in the solid and liquid states is given by two horizontal lines erected at their respective melting points, extending from one component to the other; if the liquidus and solidus curves become spaced wider and wider apart, naturally they will approach, as a limit, these two horizontal lines.

much further than is warranted even in the case of liquid solutions. It is thus quite conceivable that even if the unit of homogeneity were a thousandfold larger than an elementary cell, an aqueous solution might likewise appear to be inhomogeneous, especially if the solute molecules were quite large. Let us, therefore, seek elsewhere some other criterion of the nature of a regular distribution. In the first place, it cannot be denied that some sort of chemical affinity is implicit in the tendency towards a regular distribution, because there is absolutely no reason on the basis of probability why the solute atoms can be made to distribute so regularly in the space lattice. If a regular lattice merely represents a special form of solid solution, whose free energy is at a minimum, then the perplexing question arises as to why once the regular distribution is obtained, it can be destroyed again by merely heating up to a certain temperature and cooling down rapidly.

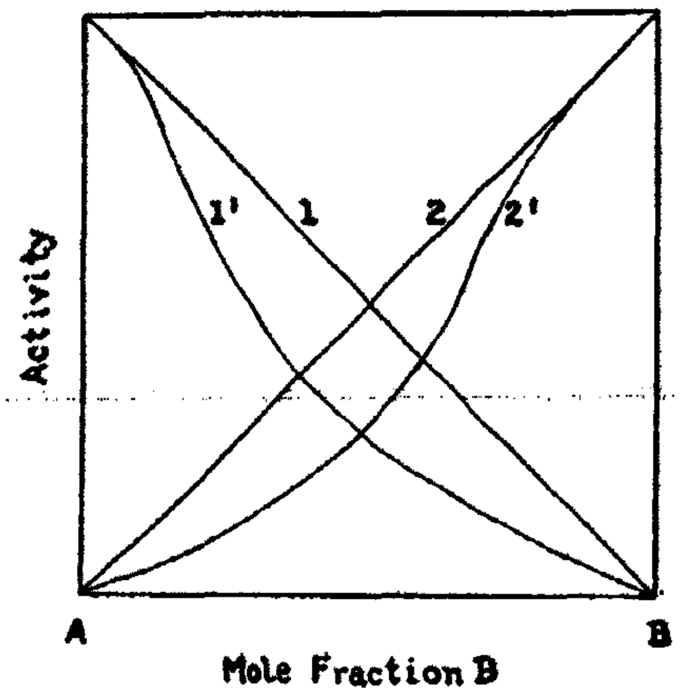

Fig. 9

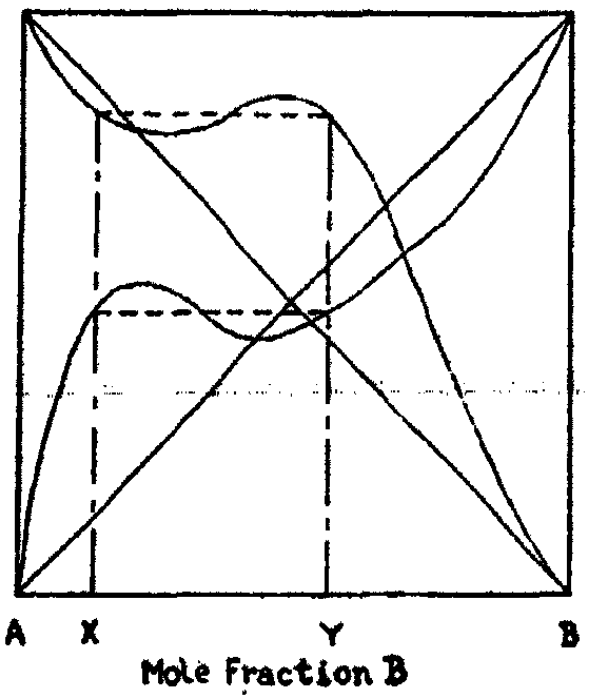

Fig. 10

Fig. 9. Activity-composition Curves

The linear activity-composition curves 1 and 2 indicate that the solid solutions are ideal from A to B. The negative deviations of the activity-composition curves 1' and 2' indicate a strong tendency to compound formation, although the compound formation is incomplete.

Fig. 10. Activity-composition Curves

The activity-composition curves indicate a tendency to compound formation between A-X and Y-B and a tendency to liquation between X-Y.

On the assumption that a regular distribution is a compound, the critical temperature then corresponds to a melting phenomenon in the solid state. When the solvent and solute atoms have some affinity for each other to form compounds, their size and shape must undergo some alteration as a result of the alteration in their electronic configurations (e.g., as due to sharing of electrons) and consequently their crystallographic habits will likewise be modified. The larger the affinity, the more marked will the alteration be, so that the compound may actually crystallize in an entirely different system, although it should be noted that often it is simply a matter of changing the crystallographic axes of reference.[9]

It is certainly curious that a solid solution, in its tendency to liquate or unmix and to form a regular structure, behaves like a dispersed system. A system in which all the dispersed particles are of the same size and therefore, possessing the same surface energy per particle, may theoretically be expected to be rather stable and should show little or no tendency towards aggregation; it is only owing to the difference in the surface energy of the dispersed particles of varying size that we have a tendency towards aggregation,[10] which may eventually lead to two equally stable states, viz., (1) a state in which the dispersed particles finally aggregate into a single large particle and (2) a state in which all particles again assume the same, though larger, particle-size. The former state is equivalent to the liquation tendency in solid solutions described above, while the latter is similar to the tendency to form a regular distribution. The writer hopes to work out these theoretical relationships in more detail in the future.

SUMMARY

1. On the basis of the results obtained in the study of some iron–silicon alloys of high purity, by means of the thermoelectric method, electrode potential measurements and x-ray crystal analysis, it is concluded that Fe_3Si (ϕ) is a compound and not merely a distinguished point in a series of solid solutions. The existence of Fe_3Si_2 (η) and FeSi (ϵ) is also indicated by the electrode potential measurements, without direct evidence, however, of their actual chemical composition.

2. By the thermodynamic method of studying the depression in the freezing point, it is shown that the actual composition of ϕ is $(Fe_3Si)_2$ or Fe_6Si_2.

3. In the hope of helping to clarify some of our conceptions regarding the stability of solid solutions, the tendency to liquation (i.e., unmixing) and formation of regular distribution, has been discussed at some length from

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[9] To illustrate: If A and B crystallize in the face-centered cubic system, but the regular distribution crystallizes in the body-centered tetragonal system with, say, $c/a = 1.5$. Then if we choose different crystallographic axes of reference for the face-centered cube and treat A and B as crystallizing in the body-centered tetragonal system with $c/a = 1.414$, the crystallographic differences become much less and more understandable.

[10] This is because the system is not in equilibrium, because although the usual parameters of the free energy (pressure, temperature, and composition) are defined, the change in the free energy with respect to the surface $(\partial F/\partial \sigma)_{P,T,N}$ has not been determined. Hence, the system will possess an additional degree of freedom.

the thermodynamic point of view. Reasons why a solid solution with a regular distribution should be treated as a compound, have been advanced.

The facilities for carrying out this investigation in the Department of Chemistry, Washington Square College of New York University, were kindly provided by Professor Ehret (who read the proof in the absence of the author), and to him and to Professor King the writer desires to express his cordial thanks for their friendly interest and suggestions during the progress of the work. Special mention should be made of the diligent assistance of Messrs. Diller and Abramson—the former for making the thermoelectric study, and the latter for taking numerous electrode potential readings.

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THE MOLECULAR WEIGHTS OF SOME DISSOLVED SUBSTANCES

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The molecular weight of a polymer of phenylacetaldehyde when it was dissolved in seven solvents, was determined by one of us, using the freezing point method (1). The molecular weight was about 360 in six solvents, indicating the molecule $(C_8H_8O)_3$, but the molecular weight was believed to be about 720 in bromoform and to indicate $(C_8H_8O)_6$. It was thought that other examples of similar behavior might be found, especially among substances which exist in different modifications in the solid state or as amorphous solids. Such has not been confirmed, except for the association of some organic acids in benzene, bromoform, and paraldehyde towards the bimolecular form,—a fact which has long been known. Moreover the high molecular weight obtained for the phenylacetaldehyde polymer in bromoform was proved to be wrong; this result was due to the bromoform being moist (or impure).

The molecular weights of the various solutes were found by Raoult's method, using Beckmann thermometers and working in a current of dry air when necesary. The approximations of the method have at least been more fully realized. Thus with aniline, for example, the supercooling was so serious that only the molecular weight of the phenylacetaldehyde polymer was determined in this solvent. And with anethole the supercooling was so serious and the subsequent rate of crystallization so slow that correct freezing points could not be obtained. Again, the lag in a Beckmann thermometer is sometimes large, or there is a slow rise of the readings after a previous exposure to a higher temperature; also the exposed-stem correction may become appreciable, and variable if the sunlight falls directly on the thermometer. While the difference in the freezing points of solvent and solution should not, with the usual apparatus, be less than 0.1°C. if results are to be obtained with an accuracy of about 2 per cent, however, even with ordinary precautions the results may vary disconcertingly; also the theoretical imperfections from Raoult's law, or from the behavior of ideal dilute solutions, may render the results approximate. The variations in Raoult's constant, as quoted from different observers for a given liquid, themselves indicate the approximations which may be expected in the molecular weights thus found (2).

In our work the following were taken as Raoult's constants, or the molecular depressions of the freezing point for 1 g. of solute in 100 g. of solvent:—benzene, 51; bromoform, 144; phenol, 72.7; acetic acid, 39, paraldehyde, 70.5; aniline, 58.7.

A new sample of phenylacetaldehyde polymer was prepared by washing away the unchanged phenylacetaldehyde with alcohol, and then by drying the residue over sulfuric acid for a month. The polymer was subsequently kept over calcium chloride. The polymer consisted of definite needle-shaped crystals (rhombic ?). Its melting point was 104.5°C. Samples of this polymer were dissolved and recrystallized, or recovered, from carbon tetrachloride, benzene, and ether, as similarly shaped crystals. The melting points of these samples were 103.5°C., 105°C., and 103.5°C., respectively, the lower values being probably the better. These samples had the same molecular weights in bromoform, benzene, and phenol within the limits of the experimental errors.

A number of experiments with bromoform indicated that the molecular weights here seemed to come high readily, or the freezing points of the solutions tended to be high, which was disconcerting as in these experiments the maximum temperatures are usually taken as the true freezing points. Thus various samples of the phenylacetaldehyde polymer gave in bromoform the molecular weights 375, 389, 393, 294, and 360. Other experiments clearly showed that with moist bromoform high results were obtained for the molecular weights, and the first three of the above results are so affected; in the fourth result the depression of the freezing point was small, but the last experiment was done with every precaution to keep the bromoform dry. The bromoform is best purified by distillation, followed by drying over potassium carbonate, and by freezing out; it remains colorless over potassium carbonate. In the above experiments the depressions varied from 0.100°C. to 0.540°C., and the concentrations from 0.26 to 1.46 g. of solute per 100 g. of solvent.

In aniline the phenylacetaldehyde polymer had the molecular weight of 335, this value being corrected for the supercooling (1.6°C.) of the solution, the concentration of which was 0.706. This solvent not only gave excessive supercooling but was also extremely hygroscopic.

In phenol and in acetic acid the phenylacetaldehyde polymer also existed in the trimolecular form, which therefore was its constant form in all the solvents examined.

Paraldehyde was found to be trimolecular in benzene, phenol, bromoform, and acetic acid; it is also trimolecular in water (3).

Metaldehyde was prepared from acetaldehyde; its melting point in a sealed tube was 140°C. Unfortunately it was not soluble in the solvents at

TABLE 1

Molecular weights found

The concentrations of the solutions (grams of solute per 100 g. of solvent) are given in parentheses.

SOLUTE	EMPIRICAL M	SOLVENT				
		Benzene	Bromoform	Phenol	Acetic acid	Paraldehyde
Phenylacetaldehyde polymer	120	356 M_3 (1.3–2.0)	360 M_3 (0.2–1.5)	368 M_3 (0.86)	363 M_3 (0.60)	403 M_3 (0.38)
Paraldehyde	44	132 M_3 (3.66)	128 M_3 (0.24–0.6)	123 M_3 (0.78)	138 M_3 (1.58)	—
Anisaldehyde	136	142 M (2.1)	149 M (0.57)	145 M (0.82)	148 M (1.90)	—
Cinnamaldehyde	132	136 M (1.3–2.4)	148 M (0.43)	133 M (0.48)	114 M (0.89)	—
Benzophenone	188	168 M (6.93)	173 M (0.39)	187 M (0.78)	192 M (0.93)	181 M (1.04)
Phthalic anhydride	148	—	—	160 M (0.66)	156 M (0.85)	160 M (0.43)
Cinnamic acid	148	264 M_2 $\rightleftharpoons$ (0.53) M	302 M_2 (0.27)	161 M (1.03)	149 M (1.3–0.6)	243 M_2 $\rightleftharpoons$ (0.43) M
Phenylacetic acid	136	217 M_2 $\rightleftharpoons$ (1.04) M	269 M_2 (0.59)	153 M (1.40)	150 M (1.50)	214 M_2 $\rightleftharpoons$ (1.04) M
Benzoic acid	122	244* M_2 (1–4)	254 M_2 (0.49)	137 M (1.26)	136 M (1.57)	194 M_2 $\rightleftharpoons$ (0.97) M
Rhombic sulfur	32	242 M_8 (1.04)	253 M_8 (0.18)	—	—	—
Monoclinic sulfur	32	260 M_8 (0.45)	246 M_8 (0.45)	—	—	—

* Roloff: (1895). See Seidell's Solubilities of Inorganic and Organic Substances.

our disposal, except in phenol. In phenol three experiments, at concentrations 0.659, 0.655, and 0.578, gave the molecular weights 165, 146, and 147—mean = 153; this is just about the mean between the trimolecular and the tetramolecular forms.

Paraformaldehyde was dried over sulfuric acid for days: it was apparently crystalline under the microscope. It melted in a closed tube at 155–160°C., resolidifying on cooling; it sublimed from about 135°C. in the closed tube. It was insoluble in the usual solvents, but it dissolved in phenol slowly, giving a strong smell of formaldehyde. The molecular weight in phenol (concentration = 0.65) was 35, indicating complete dissociation ($CH_2O = 30$).

Anisaldehyde and cinnamaldehyde were unimolecular in all the solvents examined, as also were phthalic anhydride and benzophenone. The ordinary stable form of the latter substance was used.

Rhombic and monoclinic sulfur were examined in benzene and in bromoform; in both of these solvents, however, the sulfur is not readily soluble. The depressions of the freezing point were small, but they indicated octatomic molecules, S_8, in both solvents for both solutes.

Benzoic, cinnamic, and phenylacetic acids behaved similarly. In benzene, bromoform, and paraldehyde these acids were partly associated, nearly completely to the bimolecular stage in the first two solvents, and about half-way to that stage in the paraldehyde. But it is well-known that their degrees of association depend on the concentrations in solution. In phenol and in acetic acid, however, these three acids were (within the limits of error) unimolecular.

Table 1 gives the chief results. Here the molecular weights obtained are quoted, with the concentrations (g. of solute per 100 g. of solvent) set underneath in brackets and showing where duplicate experiments or more were done; also the molecules existing in the solutions are indicated.

The authors wish to thank the Council for Scientific and Industrial Research, Australia, for a grant towards the expenses of the investigation.

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NEW BOOKS

Matiere et Energie. By Victor Henri. 436 pp. Paris: Hermann et Cie, 1933. Price: 110 francs, unbound.

The influence of the new molecular physics is constantly felt with increasing and expanding force both by the layman and also within the realms of science itself. It is not a cause for wonder that men of science feel attracted to the subject with such force as often to be impelled to record the results of the new acquisitions in book form, even when in a field in which they may not previously have been actively engaged.

That Victor Henri, so well-known for his contributions to spectroscopy and photochemistry, has succeeded in presenting a laudable monograph in molecular physics, there will be no doubt on the part of the reader. He has approached the subject from a charmingly individual and philosophical point of view and maintains throughout a closeness of contact with the other more classical fields of chemistry and physics which convince the reader of the breadth of his grasp of the subject in its entirety.

The subjects treated are: the discontinuity of matter—determination of the number of molecules; the chemical elements and the properties common to all elements—Roentgen spectra, atomic number; the periodic system; radioactive elements, isotopes; disintegration and synthesis of elements—their spatial properties in solids and liquids; the kinetic gas theory; the structure of atoms, including a splendid history of the subject from pre-Bohr theories to those of the present time.

In the chapter on isotopes an extended table giving the hypothetical constitution of nuclei according to Heisenberg is given and the supposed ratio of neutrons:protons in each species of element.

In a work apparently quite free from errors one is surprised to find—in at least two citations—the discovery of the refraction of electrons credited to Davison and Kunsman instead of to Davison and Germer.

S. C. Lind.

Die Alkalichloridelektrolyse in Diaphragmzellen. Eine Theoretische und Experimentelle Untersuchung. Part I. By Gosta Angel. 126 pp. Berlin: Verlag Chemie, G. M. B. H., 1933. Price: 12 M.

This book, which is divided into four parts, represents a four year investigation on alkali chloride electrolysis in diaphragm cells. The work was carried on in the electrochemical laboratory of the Kgl. Technische Hochschule at Stockholm.

Part I (37 pp.). A general review of the subject, including the work of other investigators. A detailed presentation of the theory is made and a number of equations are given for estimating the quantitative relations existing between the rate of flow of sodium chloride, the current flowing, the current yield in sodium hydroxide in per cent, the moles of chloride per liter in the anolyte and catholyte, and the transference number of the cation. This material is clearly presented with the aid of ten curves and seven tables of data.

Part II (32 pp.) Experimental results. A detailed picture of the experimental cell and analytical methods used is given, together with nine tables of data and three curves. The experimental results served to test the theoretical equations given in Part I. Much careful work was done and good agreement with the theory was found.

Part III (24 pp.). Eleven tables and nine curves are used to present the properties of the sodium chloride and sodium hydroxide solutions giving the specific gravity, the relative viscosity, and specific conductivity of various concentrations of salt solutions at temperatures from 18°C. to 70°C. The influence of these variables on cell operation is discussed in considerable detail.

Part IV (20 pp.). In this section the author gives equations and data for the electrolysis of potassium chloride solutions. Three curves and seven tables of data are given. The general nature of the equations for potassium chloride is similar to those for sodium chloride, but the quantitative results are somewhat different These differences are carefully defined and clearly explained.

This book combines a nice presentation of theory with careful experimental work. The many curves and tables summarize and coördinate the material into a readily usable form which will be of interest not only to scientific workers but also to those engaged in the commercial applications of alkali chloride electrolysis.

G. H. Montillon.

The Scientific Achievements of Sir Humphry Davy. By Joshua C. Gregory, B. Sc., F. I. C. 12.5 x 19 cm.; vii + 144 pp. New York: Oxford University Press, 1930. Price: $2.00.

This compact little volume is an exposition of Davy's experimental and theoretical contributions. Although it does not, like certain other biographies, trace in detail the entire course of Davy's life, it does introduce in chronological sequence enough well-chosen biographical material to explain the origin of the great conceptions which developed in Davy's mind.

In his first paper, written at the age of nineteen years, Davy had the temerity to oppose certain aspects of Lavoisier's theory of combustion. To explain the light which accompanies rapid combustions, the youthful chemist postulated the existence of *phosoxygen*, a compound of oxygen and light; the accompanying heat he regarded as a "repulsive motion" of particles. The outstanding investigation at Dr. Beddoes' Pneumatic Institution was the famous study of the physiological properties of nitrous oxide. Readers who have a sense of humor will heartily enjoy the author's paragraphs on the behavior of Davy's "patients."

Before discussing Davy's astonishing electrochemical successes, the author describes the state of consternation which resulted from Nicholson and Carlisle's decomposition of water with the voltaic pile. To a contemporary, the evolution of hydrogen and oxygen from *separated* wires seemed utterly incomprehensible. When the two poles of the battery were placed in separate vessels connected by a siphon, "the oxygen and hydrogen still fizzed off separately... When oxygen streamed off at one wire, the hydrogen with which it had been combined had apparently to scamper through the siphon to stream off at the other wire." Davy's experiments led him to a rational explanation of this phenomenon and the isolation of the alkali and alkaline earth metals. Since many properties of the metals could be explained by assuming that they contain hydrogen, Davy pondered over, but did not adopt, a revised phlogiston theory in which this hypothetical principle of flammability was identified with hydrogen.

After reading of the difficulties which Davy had to overcome in order to prove the elementary nature of "oxymuriatic acid," one readily understands what a revolution in chemical thought is implied in the words "chlorine" and "hydrochloric acid." The paragraphs on the safety-lamp for miners show the lofty side of Davy's character as he "refused to put 'four horses' to his 'carriage' by patenting his invention." The chapter on Davy and Dalton is an interesting character study. Although Davy avoided the word "atom" because it implies indivisibility, he honored Dalton for "fixing the *proportions* in which bodies combine."

Since the volume makes possible a truer and fuller appreciation of the mental acumen of Sir Humphry Davy, it should prove to be of permanent value to chemists.

MARY ELVIRA WEEKS.

La Structure de la Cellulose dans ses Rapports avec la Constitution des Sucres. By G. CHAMPETIER. 16.5 x 25 cm.; 28 pp. Paris: Hermann et Cie, 1933. Price: 8 francs.

This little booklet is an excellent concise review of the present state of our knowledge regarding the structure of cellulose and its parent sugar, glucose. A brief historical review of the development of the structure of glucose ending with the work of Haworth and his school on the structures of stable and labile glucose is followed by a discussion of the new structural formulas of glucose and cellobiose proposed by Haworth. The second part of the monograph dealing with the structure of cellulose discusses celluloses from different sources, the hydrolysis of cellulose, and the light shed on the problem by x-ray crystal studies of Sponsler and Dore, and Meyer and Mark. The form and length of the hexose chains and their arrangement in cellulosic fibres is discussed, followed by a brief review of the principal reactions of cellulose and their relation to the proposed structure. The final section is devoted to the dimorphism of cellulose, in which field the author has made contributions. Although presenting nothing essentially new, this little monograph is valuable reading for anyone wishing a collected modern view of the evidence relating to the structure of this important polysaccharide.

RALPH E. MONTONNA.

Thermodynamics. By ALFRED W. PORTER, D. Sc., F. R. S. viii + 96 pp.; 22 figures. New York; E. P. Dutton and Co., Inc., 1931.

This small volume is one of a series of monographs on physical subjects and is written by an expert for students of physics rather than for students of chemistry. The introductory chapters dealing with the historical development of the subject are possibly the most useful portions of the book. They could be read with profit even by those who consider themselves well acquainted with thermodynamics.

F. H. MACDOUGALL.

An Outline of Wave Mechanics. By N. F. MOTT. 155 pp. Cambridge, England: The University Press, 1930.

The author attempts in eight short chapters to deal with the new wave mechanics, and it is remarkable that he can condense such a wealth of information into such a small space! He succeeds remarkably well, although he abbreviates the mathematical treatment at times just at the place where the non-mathematical reader would want more details. However in such places ample references are given so that the interested student can follow up the subject if he has the perseverance and the necessary mathematical skill. Moreover the author states in his introduction that he has written the book for advanced students in physics and for research workers. The eight chapters cover the following subjects: I. Waves and Particles II. The Wave Equation. III. Group Velocity and the Uncertainty Principle. IV. The Theory of Stationary States. V. The Absorption of Radiation. VI. The Helium Atom and the Hydrogen Molecule. VII. Dynamics of Systems Containing Many Electrons. VIII. The Spin of the Electron and the Exclusion Principle. The book is quite convenient as a reference volume. A few printer's errors will give no trouble to the interested reader.

GEORGE GLOCKLER.

Grundbegriffe der Chemie. By E. RABINOWITSCH. 151 pp.; 2 figs. Sammlung Goeschen. Berlin and Leipzig: Walter de Gruyter and Co., 1930.

The fundamentals of chemical thought are told in as concise a manner as is possible in such short space. This forced brevity makes the book of little value to the uninitiated, but the reader conversant with physical and chemical thought will find the little volume an interesting review of chemical theory. It should be of especial interest to American students of chemistry who wish to improve their knowledge of chemical German, for the style is very clear and the book maintains the high standard of this collection of scientific writings.

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The Quantum Theory. By FRITZ REICHE. Translated from the German by H. S. Hatfield and H. L. Brose. London: Methuen & Co., Ltd., 1931.

This little volume contains an excellent treatment of the earlier quantum theory, —Planck to Bohr. It is very readable and should serve well students who wish to become acquainted with the earlier developments. The additional notes and references are very helpful and anyone desirous of studying in the field of modern theoretical atomic and molecular physics could well start his course with this volume. No attempt is made to take the newer theories of wave mechanics into account, although they are introduced in the later chapters and a sufficient number of references are given to enable one to go to the original literature. Moreover, individuals already acquainted with the topics dealt with will enjoy the treatment accorded the subject, and it is well worth anyone's time to read this book.

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Die Chemische Emissions Spektralanalyse. By W. GERLACH AND E. SCHWEITZER. 120 pp; 35 figures. Leipzig: Verlag von L. Voss, 1930.

The authors cover mostly their own work and experience in the spectroscopic analysis of metals. The fundamental principles and the equipment used in both qualitative and quantitative procedure are discussed in seven chapters. The reader can get a fair idea of both the successes and the difficulties of this mode of analysis.

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Vorlesungen über Wellenmechanik. By A. LANDE. 132 pp.; 15 figures. Leipzig: Akademische Verlags Gesellschaft m. b. H., 1930.

These lectures were given by Professor Lande at the Ohio State University, Columbus, Ohio, and cover the field as it had been developed at the time. Since so many topics are treated it follows that the statements of individual problems are very brief, and the book should be most satisfactory to the student who already has a good knowledge of this branch of modern physics. Anyone building a library on quantum mechanics will be glad to add this summary of the subject to his collection, and to use it as a reference book.

GEORGE GLOCKLER.

Les Théorèmes de Conversation dans la Théorie des Chocs Électroniques. By L. GOLDSTEIN. 26 pp. Monograph No. 70 of the scientific and industrial series published by Hermann & Co., Paris, 1933.

This volume is the ninth of the series on theoretical physics published under the direction of Professor L. de Broglie. The author shows by the mathematical methods of wave mechanics, using Born-Dirac collision theory, that the laws of conservation of energy and momentum are contained within the frame-work of these theories.

GEORGE GLOCKLER.

A STUDY OF THE EFFECT OF SALTS ON THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY COLLOIDAL PLATINUM

MERLE A. HEATH AND JAMES H. WALTON

Laboratory of General Chemistry, University of Wisconsin, Madison, Wisconsin

Received March 17, 1933

ERRATUM

Vol. XXXVI, No. 1

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It appeared that some knowledge of the changes in the surface of the colloid could be gained by measuring the change in migration velocity of the particles in an electric field. In this way it might be shown what relation exists between adsorption of ions by the colloid and the change in the catalytic activity.

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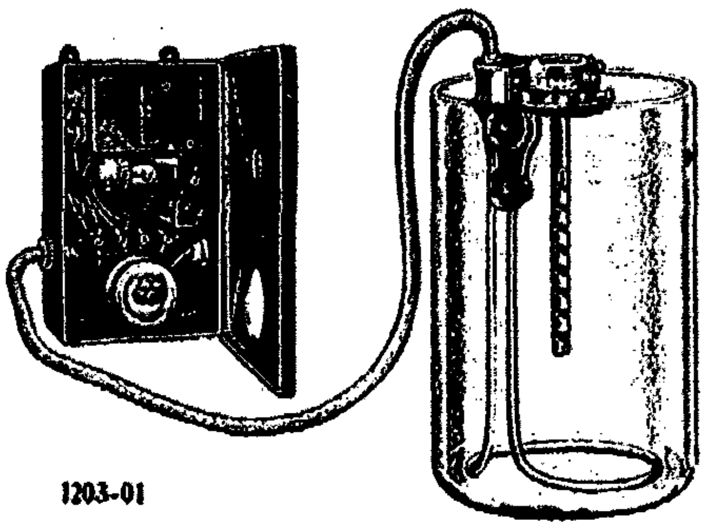

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Although there have been numerous studies (1) of the catalytic decomposition of hydrogen peroxide by various colloidal systems, the effect of neutral salts has been investigated in detail in only a few cases. Lottermoser and Lehmann (2) studied the effect of a number of neutral salts and hydroxides on the catalysis of the reaction by colloidal manganese dioxide. In this laboratory, Kepfer and Walton (3) investigated the effect of electrolytes on the catalytic decomposition by colloidal ferric oxide. Except for the work of Kastle and Loevenhart (1) no extensive study seems to have been made of the effect of electrolytes on the catalytic decomposition of hydrogen peroxide by an electrocolloid of the type of Bredig's platinum sol.

In the case of colloidal ferric oxide, Kepfer and Walton obtained results which indicate that there is a general retarding effect of neutral salts which is connected with their adsorption on the surface of the colloidal particles. It does not seem to be conclusively established, however, that this is a general effect of neutral salts on all colloidal catalysts. With colloidal manganese dioxide, Lottermoser and Lehmann state that the addition of alkali salts in considerable concentration exerts only a feeble retardation on the decomposition of hydrogen peroxide. Bredig and his coworkers (4), in studying the catalysis by several electrocolloids, found some salts to be effective and others ineffective.

The present investigation was undertaken to study in some detail the effect of various salts on the catalytic decomposition of hydrogen peroxide by colloidal platinum, and to determine, if possible, whether a general adsorption effect is obtained (as with colloidal ferric oxide) or a specific effect which might be attributed to the chemical constitution of the colloid surface.

It appeared that some knowledge of the changes in the surface of the colloid could be gained by measuring the change in migration velocity of the particles in an electric field. In this way it might be shown what relation exists between adsorption of ions by the colloid and the change in the catalytic activity.

EXPERIMENTAL

Reagents

The colloidal platinum solution was prepared by Bredig's method. The sol was allowed to stand for several days and then siphoned off to remove the precipitated particles. A portion of the stock solution was diluted to a concentration convenient for use in the experiments and was preserved in a thoroughly steamed-out Pyrex flask. This diluted portion was used in all the experiments.

The hydrogen peroxide was Merck's "reagent" quality superoxol, redistilled in an all-quartz system under reduced pressure, diluted with conductivity water to approximately 0.25 *M*, and kept in quartz flasks. All the water used was prepared in a conductivity water still, then redistilled in a quartz apparatus, and kept in steamed-out Pyrex flasks.

Method of procedure

The reaction was carried out at 25°C. in Erlenmeyer flasks, which were repeatedly cleaned and steamed before using. A definite order of adding the reagents was adhered to, since, as will be shown later, it has an effect on the rate of decomposition in certain cases. Thirty-five cc. of hydrogen peroxide solution was first placed in the flask, followed by 2 cc. of electrolyte solution of the concentration desired. After a few minutes 1 cc. of the platinum sol was added, and the solution thoroughly mixed by shaking. After 1 minute 4 cc. was titrated in acid solution by standard potassium permanganate. This was taken as the titration at zero time, and similar titrations were made at 15 minute intervals. Two or more duplicate runs were made on each solution. Velocity constants for a unimolecular reaction were calculated, and the time required for 50 per cent decomposition of the hydrogen peroxide was obtained.

MEASUREMENT OF THE VELOCITY OF MIGRATION OF THE COLLOIDAL PARTICLES IN AN ELECTRIC FIELD

The stability of a lyophobic sol is almost entirely due to a potential difference between an adsorbed surface layer and a relatively diffuse surrounding layer of oppositely charged ions. The migration velocity of the particles in an electric field is directly connected with this stabilizing potential, so that these measurements give quantitative information in regard to the stability of the system. Kepfer and Walton (3) employed flocculation methods to follow the change in stability of their colloidal catalyst, ferric oxide. However, with colloidal platinum, in order to have the reaction slow enough to be measured accurately, the sol must be so dilute that flocculation values are not conveniently determined by macroscopic observation. In an effort to determine if the concentration of electrolyte corresponding to the flocculation value had any distinctive effect (as is the case with colloidal ferric oxide) on the velocity of decomposition of hydrogen peroxide, flocculation values were run on the concentrated sol. The migration velocity of the particles of the concentrated sol in the presence of the concentration of electrolyte corresponding to the flocculation values was then determined, using an ultramicroscopic method (5). The results are given in table 1 and show the close connection between the flocculation and migration methods as means of determining the stability of colloidal platinum.

TABLE 1

Relation between migration velocity and flocculation value (concentrated platinum sol)

ELECTROLYTE		BY OBSERVATION AFTER 10 HOURS	MIGRATION VELOCITY
	millimols per liter		*mu/sec./v./cm.*
NaCl	0		−3.3
	1	Stable	
	2	Stable	−2.5
	3	Stable	
	4	Partially flocculated	−2.2
	5	Flocculated	−2.0
	10	Flocculated	
$BaCl_2$	0.05	Stable	
	0.06	Stable	−2.1
	0.08	Flocculated	−1.9
	0.10	Flocculated	
	0.20	Flocculated	
	0.50	Flocculated	
$AlCl_3$	0.004	Flocculated	
	0.006	Flocculated	
	0.01	Flocculated	
	0.02	Flocculated	
	0.04	Partially flocculated	+1.9
	0.06	Stable	+2.2
	0.08	Stable	

With both sodium chloride and barium chloride the migration velocity corresponding to the flocculation value is approximately −2 mu per second per volt per centimeter (the sol being negatively charged). This velocity corresponds to a "critical" potential of about 30 millivolts. In the case of aluminum chloride the smallest concentration used has already reduced the migration velocity below this critical value, and the sol was flocculated. With increasing concentration of aluminum chloride the colloidal platinum again became stabilized as a positively charged sol. This stabilization apparently took place when the positively charged colloidal particles had a migration velocity of about 2 mu per second per volt per centimeter. All the results obtained here not only agree with the postulate of Powis (6) that it is not necessary to deprive the particles of lyophobic colloids completely of their charge to cause flocculation, but also show that in order to have a stable platinum sol it is necessary to have sufficient electrolyte adsorbed to contribute a potential difference of over 30 millivolts.

The platinum sol was diluted to the concentration of the decomposition experiments and measurements of the migration velocity of the colloidal particles were taken over the same range of concentration with each of the electrolytes whose effect on the catalytic decomposition of hydrogen peroxide was studied. In this way the change in the migration velocity could be directly compared with the effect on the rate of decomposition of the hydrogen peroxide.

It has been concluded that at a migration velocity of -2 mu per second per volt per centimeter, the platinum sol enters a region of instability where it will flocculate on standing. It is evident from all of the curves that this point lies on a curve of increasing retardation but is of no unusual significance in the effect of the electrolyte on the catalytic decomposition of hydrogen peroxide.

EXPERIMENTAL RESULTS

The decomposition of hydrogen peroxide as catalyzed by colloidal platinum was studied in the presence of both the chlorides and nitrates of sodium, aluminum, and thorium, and in the presence of barium chloride. The change in migration velocity of the same concentration of platinum sol in conductivity water, with addition of the above salts, was also determined. The results are tabulated below in tables 2 to 5, and represented graphically in the accompanying figures 1 to 5. In the figures the concentration of electrolyte in millimols per liter is plotted against the time for 50 per cent decomposition in the case of hydrogen peroxide decomposition, and against mu per second per volt per centimeter in the case of the migration velocity of the colloidal particles in an electric field.

Effect of sodium salts

The first experiments on the effect of electrolytes on the catalysis were made with a univalent ion, sodium. Data (table 2) were obtained for both sodium chloride and sodium nitrate. The effects of sodium nitrate and sodium chloride on the rate of decomposition of the hydrogen peroxide are illustrated in figures 1 and 2, respectively, where they are compared with the effects of the same salts on the migration velocity of the colloidal particles. It is evident that up to a certain point these two effects correspond rather closely, and it may be deduced that within this concentration range the effect is similar to that found by Kepfer and Walton for

TABLE 2

Effect of sodium salts on the decomposition of hydrogen peroxide by colloidal platinum and on the migration velocity of the colloidal particles

ELECTROLYTE		AVERAGE 0.4343*K*	TIME FOR 50 PER CENT DECOMPOSITION	MIGRATION VELOCITY
	millimols per liter		*minutes*	*mu/sec./v./cm.*
NaCl	0	0.01258	24	−2.8
	1			−2.1
	2.63	0.00512	58.8	−2.0
	5			−1.7
	6.58	0.00398	75.7	−1.7
	9.9	0.00367	82.1	−1.6
	13.2	0.00333	90.5	−1.6
	17.1	0.00291	104	−1.6
	21.1	0.00248	121	−1.6
	26.3	0.00210	143	−1.6
	50			−1.5
NaNO$_3$	0	0.01046	28.8	−2.8
	1.31	0.00491	61.4	−2.1
	2.63	0.00465	64.7	−1.8
	5.26	0.00436	69.0	−1.6
	10.5	0.00452	66.6	−1.4
	13.2	0.00448	67.2	−1.4
	17.1	0.00432	69.7	−1.4
	21.1	0.00410	73 5	−1.4
	26.3	0.00366	82.3	

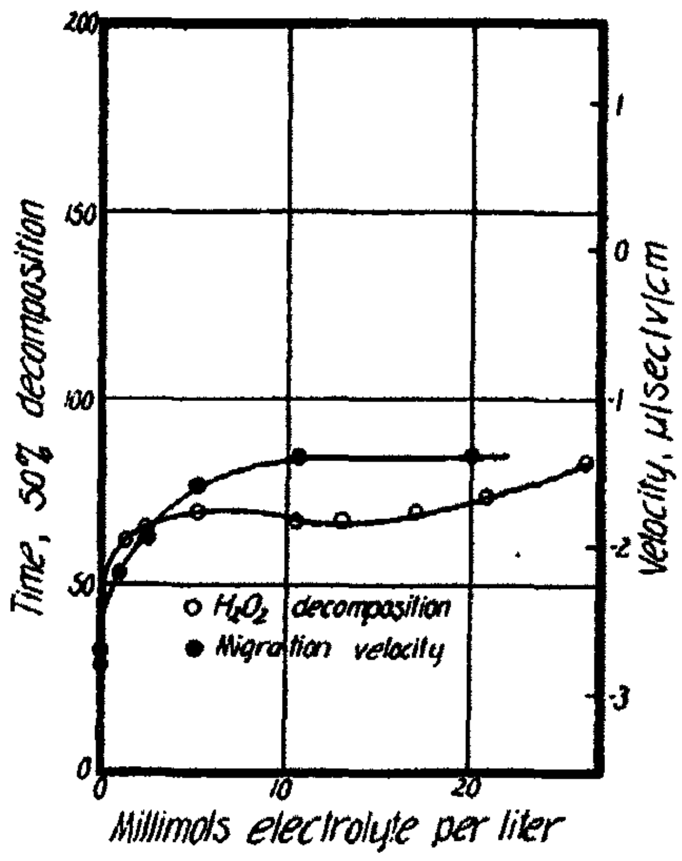

FIG. 1

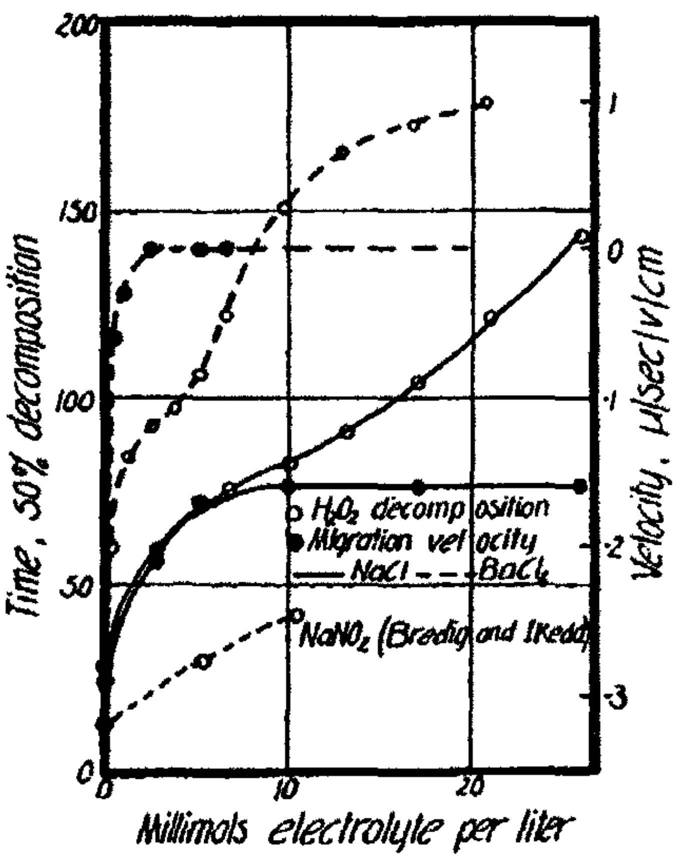

FIG. 2

FIG. 1. SODIUM NITRATE

FIG. 2. SODIUM CHLORIDE AND BARIUM CHLORIDE

colloidal ferric oxide, and that the hydrogen peroxide decomposition is decreased or retarded because of modifications in the surface ionization of the colloid.

With concentrations of sodium salts greater than 7 or 8 millimols per liter there is very little further change in the migration velocity of the colloidal particles. In the presence of sodium chloride, however, the retardation of the hydrogen peroxide decomposition continues to increase in practically a straight-line relationship. With sodium nitrate the retarding effect increases very little. This latter effect on the decomposition is, then, apparently due to the anion of the electrolyte added.

TABLE 3

Effect of barium chloride on the decomposition of hydrogen peroxide by colloidal platinum and on the migration velocity of the colloidal particles

BARIUM CHLORIDE	AVERAGE 0.4343K	TIME FOR 50 PER CENT DECOMPOSITION	MIGRATION VELOCITY
millimols per liter		*minutes*	*mu/sec./v./cm.*
0	0.01249	24.1	−2.8
0.025			−2.5
0.03			−2.1
0.04			−1.9
0.05			−1.5
0.10			−1.2
0.50			−0.6
1.0			−0.3
1.32	0.00358	84.2	Isoelectric
2.63	0.00326	92.4	Isoelectric
3.95	0.00310	97.1	Isoelectric
5.26	0.00283	106	Isoelectric
6.58	0.00248	122	
9.9	0.00200	151	
13.2	0.00181	166	
17.1	0.00174	173	
21.1	0.00169	179	

Effect of barium chloride

The effect of this bivalent chloride is similar to that of sodium chloride. The results are given in table 3 and figure 2. Barium ions are more strongly adsorbed than sodium ions, and the retarding of the rate of decomposition of hydrogen peroxide is consequently greater. Below a concentration of about 4 millimols of barium chloride per liter the curves for hydrogen peroxide decomposition and migration velocity distinctly show that there is a connection between the two effects. At higher concentrations the colloidal particles are isoelectric, but the same further retarding of the catalysis of the hydrogen peroxide decomposition that was obtained with sodium chloride is evident here; the retarding effect decreases, however, at the higher concentrations.

Effect of aluminum salts

The effect of neutral univalent and bivalent salts has been shown. Since the salts of all trivalent and tetravalent metals are hydrolyzed in solution it was not possible to compare them directly with the neutral salts. A change in pH of the solution would presumably introduce complications. Even so, the effect of these salts on the catalysis was of interest. Aluminum was chosen as a typical trivalent metal, and experiments were made using both aluminum chloride and aluminum nitrate (table 4 and figures

TABLE 4

Effect of aluminum salts on the decomposition of hydrogen peroxide by colloidal platinum and on the migration velocity of the colloidal particles

ELECTROLYTE		AVERAGE 0.4343K	TIME FOR 50 PER CENT DECOMPOSITION	MIGRATION VELOCITY
millimols per liter			*minutes*	*mu/sec./v./cm.*
$AlCl_3$	0	0.01236	24.3	−2.8
	0.002			+1.1
	0.004			1.3
	0.011	0.00337	89.4	2.2
	0.021	0.00314	95.9	2.8
	0.029	0.00258	117	3.4
	0.040	0.00303	99.4	3.3
	0.050	0.00310	96.7	2.8
	0.066	0.00304	99.0	2.9
	0.105	0.00257	117	3.0
	0.158	0.00240	125	3.4
	0.237	0.00222	136	3.1
	0.316	0.00210	144	2.7
	0.526	0.00189	159	2.5
	0.79	0.00169	178	2.5
	3.95	0.00076	396	2.5
	6.58	0.00059	510	2.4
$Al(NO_3)_3$	0.005	0.00335	89.9	
	0.011	0.00327	92.1	2.6
	0.040			3.9
	0.053	0.00295	102	3.8
	0.105	0.00322	93.4	3.1
	0.12			2.8
	0.158	0.00404	74.5	3.1
	0.211	0.00363	82.9	2.9
	0.368	0.00400	75.3	2.6
	0.526	0.00415	72.6	2.6
	0.79	0.00437	68.8	2.6

3 and 4). These salts are apparently about equally hydrolyzed, the pH of $M/1000$ aluminum chloride being 3.6 and of $M/1000$ aluminum nitrate 3.7. Any difference, in their effect, therefore, should not be due to a difference in acidity.

As expected, the aluminum salts are effective in a much lower concentration range than sodium or barium salts. At the lower concentrations the courses of the curves, represented in figures 3 and 4, are peculiar, and are probably affected by the operation of several factors, such as adsorption, ion exchange, and hydrolysis. It is to be noted, however, that in general the same kind of change in the first part of the curves is shown both in the rate of hydrogen peroxide decomposition and in the migration velocity.

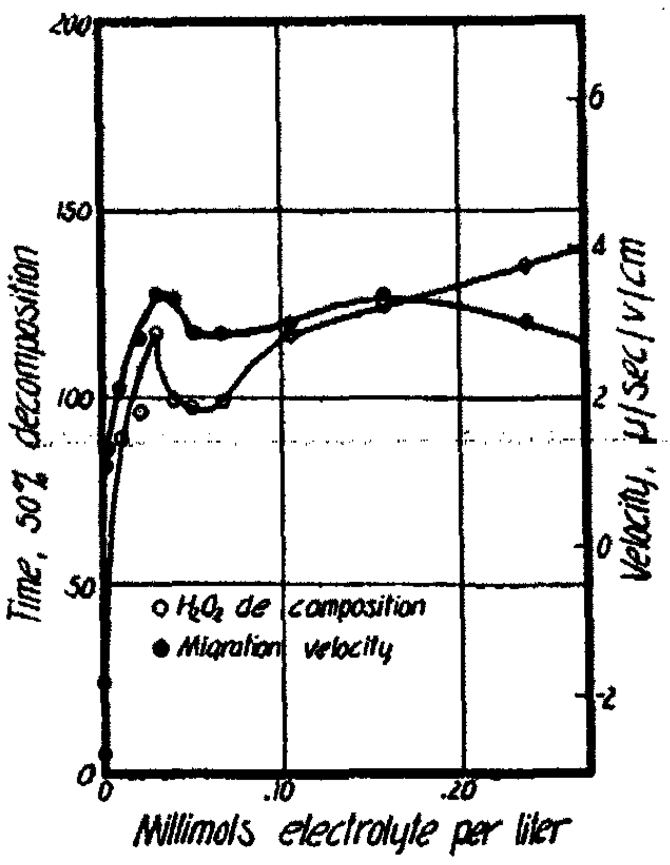

FIG. 3. ALUMINUM CHLORIDE

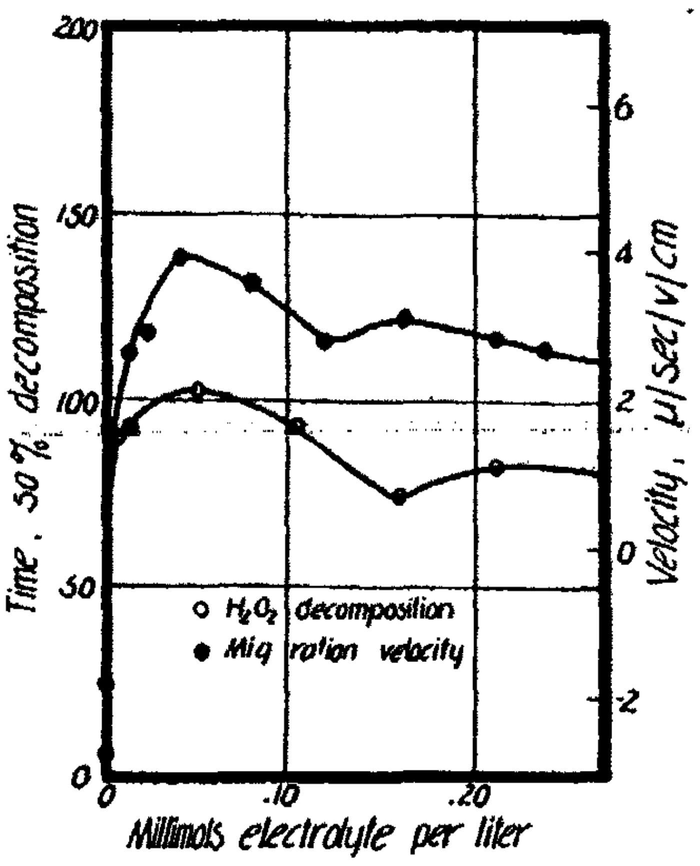

FIG. 4. ALUMINUM NITRATE

Aluminum ions are so strongly adsorbed that the colloidal system is stable as a positively charged sol during almost the entire range of concentration measured here. The slower rate of decomposition of this positively charged sol demonstrates that it is the condition of the colloid surface rather than its stability which is most important in catalyzing the decomposition of hydrogen peroxide.

At higher concentrations the same difference between the effect of aluminum chloride and aluminum nitrate on the rate of hydrogen peroxide decomposition is shown that was obtained with sodium chloride and sodium nitrate. The effect of aluminum nitrate on the decomposition velocity follows the migration velocity curve rather closely throughout the whole range of concentration measured here. With aluminum chloride the retarding effect follows the change in migration velocity only in the first part of the curve, and then shows a continual increase which apparently has no connection with the change in migration velocity. As can be seen from the data in table 4, the retarding effect is still increasing at higher concentrations than are shown in figure 3.

Effect of thorium salts

Results of experiments with the tetravalent salts, thorium chloride and thorium nitrate, are given in table 5 and figure 5.

TABLE 5

Effect of thorium salts on the decomposition of hydrogen peroxide by colloidal platinum and on the migration velocity of the colloidal particles

THORIUM SALTS		AVERAGE 0.4343K	TIME FOR 50 PER CENT DECOMPOSITION	MIGRATION VELOCITY
	millimols per liter		*minutes*	*mu/sec./v./cm.*
$ThCl_4$	0	0.01216	24.8	−2.6
	0.026	0.00654	46.1	+4.8
	0.053	0.00540	55.9	4.6
	0.079	0.00468	64.4	4.5
	0.158	0.00333	90.4	4.2
	0.237	0.00251	120	4.2
	0.368	0.00200	151	4.1
	0.526	0.00155	194	4.1
	1.0			3.8
$Th(NO_3)_4$	0	0.01216	24.8	−2.6
	0.011	0.01138	26.5	
	0.026	0.01093	27.6	+3.9
	0.040	0.01309	23.0	3.9
	0.053	0.01457	20.7	3.9
	0.079	0.01471	20.5	3.8
	0.105	0.01444	20.8	3.8
	0.290	0.01579	19.1	3.4
	0.526	0.01653	18.3	3.4
	1.0			3.4

The effect of thorium salts on the catalytic decomposition of hydrogen peroxide does not show the close relation to their effect on the migration velocity of the colloidal particles that characterizes aluminum salts. Thorium ions have a greater effect on the migration velocity than aluminum ions, but this may be due to the greater valence of the thorium ion, and aluminum ions may actually be more strongly adsorbed on the colloid surface, thus exerting a greater retardation on the catalysis. Thorium ions should, nevertheless, show some retarding effect and, since thorium nitrate has little or none, it would seem advisable to look for further explanation. Any thorium hydroxide formed by hydrolysis does not directly decompose hydrogen peroxide, or only does so very slowly, for thorium salts alone, in the concentrations used, had a negligible effect on the hydrogen peroxide. However, it is possible that the tendency of thorium hydroxide to combine with hydrogen peroxide (7) greatly decreases the adsorption of thorium ions by the colloidal platinum. This tying up of thorium ions would not be indicated in the migration velocity measurements obtained here, since, on account of the experimental difficulties involved by the evolution of oxygen bubbles, they were not made in the presence of hydrogen peroxide.

If such a reaction is a factor, allowing the thorium salt to act on the colloidal platinum before it comes in contact with the hydrogen peroxide should give a greater retardation of the rate of decomposition. An experiment was therefore carried out in which the electrolyte was first added to the platinum sol, and the hydrogen peroxide added last. The data are given in table 6.

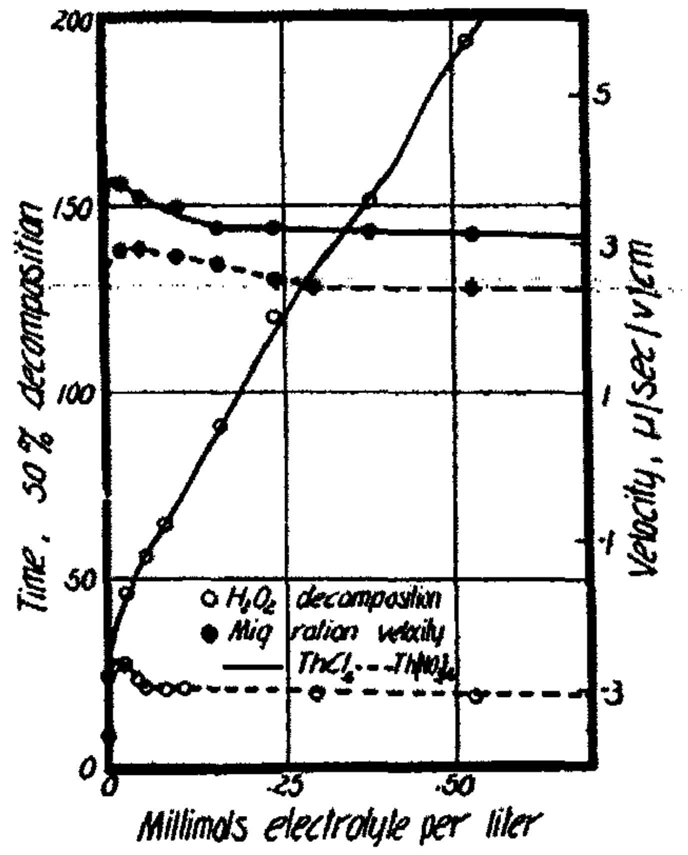

FIG. 5. THORIUM CHLORIDE AND THORIUM NITRATE

The time for 50 per cent decomposition of about 50 minutes corresponds to a 50 per cent decomposition in 20.8 minutes when the electrolyte was added to the hydrogen peroxide first. The "constants" calculated for a unimolecular reaction increase very rapidly; the constant for a zero order reaction, calculated in the last column, is much more applicable. With sodium nitrate, on changing the order of mixing in the same way, there was no difference either in the time for 50 per cent decomposition or in the velocity constant.

The results obtained in this experiment with thorium nitrate might be interpreted to indicate that the hydrogen peroxide is more strongly adsorbed under these conditions, while at the same time the rate of reaction is decreased. The rate of reaction has decreased, presumably, because the thorium salt has affected the colloidal surface. An attraction between thorium and hydrogen peroxide might, however, serve to attract the hydrogen peroxide more strongly to the surface of the platinum on which the thorium ions were adsorbed, and consequently give a change in the order of the reaction, such as was obtained here. However, the data are inadequate for any conclusions at this time.

Pennycuick (8) has found anomalous results for ferric chloride compared to aluminum salts in his study of the effect of electrolytes on colloidal platinum. He ascribes this to the much higher degree of hydrolysis of ferric chloride, so that the hydrogen ions are of primary importance rather than the extremely low concentration of ferric ions. Thorium salts are also highly hydrolyzed in solution, as the following data (9) indicate:

TABLE 6

Results obtained when thorium nitrate acts on colloidal platinum before it comes in contact with hydrogen peroxide

0.105 Millimols of thorium nitrate per liter

TIME	TITRATION	DECOMPOSED	$0.4343K_1$	K_0
minutes		*per cent*		
0	49.75	0		
15	42.15	15.28	0.00480	0.01019
30	34.15	31.36	0.00545	0.01045
45	26.65	46.43	0.00602	0.01032
60	20.00	59.80	0.00660	0.00997
75	14.70	70.45	0.00706	0.00939
90	10.95	77.99	0.00730	0.00867
Average			0.00621	0.00983
Time for 50 per cent decomposition			48.5 minutes	50.9 minutes

M/1000 solutions	*pH (glass electrode)*
$AlCl_3$	3.6
$CrCl_3$	2.8
$FeCl_3$	2.3
$ThCl_4$	2.7

The other evidence, particularly the migration velocities, does not indicate, however, that the effect of thorium salts as studied here can be considered as primarily that of the hydrogen ion.

Aside from the effect of the thorium ion, it is seen from figure 5 that thorium salts show even more distinctly than those of sodium and aluminum the difference between the effect of nitrates and chlorides on the catalytic decomposition of hydrogen peroxide by colloidal platinum.

DISCUSSION

Of the results which have been obtained here on the effect of electrolytes on the catalysis, the most striking feature is the very wide difference between the effect of chlorides and nitrates at the higher concentrations. While this might be due to the formation of free chlorine, with subsequent alteration of the catalyst surface, it is the opinion of the authors that in the concentrations used such an effect would be very small. Another explanation of this difference may involve the structure of colloidal platinum, and the mechanism of the decomposition reaction. The constitution of colloidal platinum has been the subject of thorough investigation by Pennycuick (10). He gives as the simplest formula for the sol: $(xPt \cdot yPtO_2 \cdot zPt(OH)_6)2z^- \ldots . \; 2zH^+$, Pt conventionally representing the interior of the particle, PtO_2 the oxide which covers the surface, and $Pt(OH)_6^{=}$ the stabilizing surface ionogen which is combined with part of the surface oxide, some evidence suggesting that it is bound at the surface only at active points. The weakly acidic surface oxide is converted by bases into more surface ionogens, which accounts for the protective action of univalent bases on colloidal platinum.

It has been shown by Bredig and others that the addition of a univalent base increases the rate of decomposition of hydrogen peroxide by colloidal platinum, up to a certain optimum concentration. Therefore, if Pennycuick is correct and the stabilizing effect of bases is due to the formation of more of the ionizing salt, there is apparently a close connection between the amount of this complex ion which is present on the active points of the surface and the catalytic activity of the colloid in decomposing hydrogen peroxide. It may be postulated that the decomposition of the hydrogen peroxide is actually effected by this complex in some such way as the following:

$$\left\{\begin{matrix} HO & & OH \\ HO & Pt & OH \\ HO & & OH \end{matrix}\right\}^{=} + H_2O_2 = \left\{\begin{matrix} HO & & OH \\ & Pt & \\ HO & & OH \end{matrix}\right\}^{=} + 2H_2O + O_2$$

The first step may be the formation of an unstable intermediate adsorption complex, decomposing into the above indicated products. The platinous acid may again be oxidized by hydrogen peroxide:

$$\left\{\begin{matrix} HO & & OH \\ & Pt & \\ HO & & OH \end{matrix}\right\}^{=} + H_2O_2 = \left\{\begin{matrix} HO & & OH \\ HO & Pt & OH \\ HO & & OH \end{matrix}\right\}^{=}$$

Replacement of hydroxyl radicals by other groups would destroy the effectiveness of the catalyst. Pennycuick (11) has shown that hydrocyanic acid, in the same way as bases, is removed from solution by the colloid and reacts with the weakly acidic surface oxide to produce more surface ionogens of the form $[PtO_2CN]^-$ or $[Pt(CN)_6]^=$. Unlike the univalent bases, however, hydrogen cyanide is a poison for the catalytic property of colloidal platinum. This would be expected because the ionogens now contain cyanide instead of hydroxyl radicals.

The substitution of chloride for hydroxyl in this complex would explain the retarding effect of chlorides at higher concentrations, as was found here. Since the nitrates do not easily form complex compounds in which several NO_3^- residues group themselves around a metal atom (12), the addition of nitrates should not show this retarding effect; this has been found to be true.

The fluoride ion would be expected to be inactive, since it also does not readily form complexes with such metals as platinum (13). Kastle and Loevenhart (14), studying the effect of the alkali halides, found that the fluoride did not inhibit the catalytic decomposition of hydrogen peroxide by colloidal platinum. NO_2^- residues, however, should replace the hydroxyls rather readily, and a retarding effect would be expected. Bredig and Ikeda (15) have studied the effect of sodium nitrite on the catalytic decomposition of hydrogen peroxide by colloidal platinum. Their results are plotted on figure 1 and show a considerable retarding of the catalysis.

The catalytic activity of hexahydroxyplatinic acid seems to depend on its being attached to active points of the colloid. A solution of hexahydroxyplatinic acid showed no catalytic activity, and adding hexahydroxyplatinic acid only slightly increased the activity of colloidal platinum.

The effect of salts of four different metals on the catalytic decomposition of hydrogen peroxide by colloidal platinum is, with some exceptions, very similar. The first result is a retarding of the catalysis, which follows very closely the effect of the electrolyte on the stability of the colloidal system, and which can be attributed to modifications in the colloid surface and in the ionization of the stabilizing surface complexes. This effect is practically the same as that which Kepfer and Walton have found for comparable electrolytes on the catalytic decomposition of hydrogen peroxide by colloidal ferric oxide. Thus for two different colloidal catalysts one important effect of the addition of electrolytes is to so modify the surface of the colloid that the adsorption of hydrogen peroxide is reduced and the rate of decomposition retarded.

In the case of colloidal platinum there is then a further effect due to the substitution of certain anions in the surface complex (principally $Pt(OH)_6^=$), which prevents or retards the chemical reaction by which the hydrogen peroxide is decomposed. Salts whose anions are not easily substituted in the surface complex do not show this further retarding effect.

SUMMARY

1. The catalytic decomposition of hydrogen peroxide by colloidal platinum has been investigated at a temperature of 25°C. The effect of additions of sodium chloride, barium chloride, aluminum chloride, thorium chloride, sodium nitrate, aluminum nitrate, and thorium nitrate has been studied over a considerable range of concentration, and compared with their effect on the migration velocity of the colloidal platinum particles in an electric field. A relation between the change in the rate of decomposition of hydrogen peroxide and the migration velocity of the colloidal particles has been shown.

2. Thorium salts do not show as close a relation between migration velocity of the colloidal particles and effect on the catalytic decomposition of hydrogen peroxide.

3. Evidence of a further effect of anions on the catalytic decomposition of hydrogen peroxide by colloidal platinum has been found, and a possible explanation based on substitution in the Werner complex of hexahydroxyplatinic acid on the colloid surface is advanced. The nitrate ion, which is not readily substituted in the complex, does not show this effect.

A possible mechanism for the reaction involving hydrogen peroxide and hexahydroxyplatinic acid is given.

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A RULE FOR THE EXPRESSION OF THE PARTITION OF ASSOCIATING SUBSTANCES

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The distribution of associating substances between water and various other solvents usually has been expressed by some form of the empirical equation,

$$C_x/C_w^s = K$$

where C_x represents the molar concentration of the distributed substance in the non-aqueous layer and C_w the concentration in the aqueous layer. Since the exponent of the concentration in water is not a whole number, it has little real meaning.

When distributed between water and another solvent, such as benzene or chloroform, associating substances give apparent distribution ratios with a relation to the concentration in the aqueous phase that may be expressed accurately by the equation,

$$\text{Apparent distribution ratio} = C_x/C_w = K_s\, C_w + K_i$$

The equation is that for a straight line with a slope, K_s, and an intercept, K_i. C_x and C_w refer to concentrations in moles per liter, irrespective of association or dissociation.

In figure 1 are shown a few examples of apparent distribution ratios, C_x/C_w, plotted against C_w. The data used are given by the International Critical Tables (1) and by Smith and White (2). The equation holds quite well at moderate values of C_w, as may be seen from the figure, and provides a simple means of recording and testing the experimental data. It also makes interpolation and extrapolation easier.

A similar equation may be derived upon making a few assumptions. Taking A and A_n to represent the single and the associated molecules in the y phase, respectively, and A′ and A_n' to represent the single and the associated molecules in the x phase, respectively, one may construct the following equations, according to the mass law.

$$nA \rightleftharpoons A_n \qquad K_1 = (A_n)/(A)^n$$

$$A \rightleftharpoons A' \qquad K_2 = (A')/(A)$$

$$nA' \rightleftharpoons A'_n \qquad K_3 = (A'_n)/(A')^n$$

$$C_x = n\ (A'_n) + (A')$$

$$C_y = n\ (A_n) + (A)$$

C_x and C_y may both be expressed in terms of (A) and the constants, hence,

$$C_x = nK_3K_2^n(A)^n + K_2(A)$$

$$C_y = nK_1(A)^n + (A)$$

and,

$$C_x/C_y = \frac{nK_3K_2^n(A)^{n-1} + K_2}{nK_1(A)^{n-1} + 1}$$

It is broadly established that associating substances give little or no evidence of association in water at moderate concentrations. It may be assumed, therefore, that in water the quantity, $nK_1(A)^{n-1}$, is negligible with respect to 1 and that (A) is practically equal to C_w. The equation then takes the simpler form,

$$C_x/C_w = nK_3K_2^nC_w^{n-1} + K_2$$

When the distribution ratio is a linear function of C_w, it is evident that n equals the whole number 2, and that two molecules are associated in the non-aqueous phase. In this case the equation reduces to a form similar to that of the experimental equation, namely,

$$C_x/C_w = 2K_3K_2^2C_w + K_2$$

It is of interest to mention one example, that of the partition of formaldehyde between water and chloroform, in which the equation fits the data very well when n is taken equal to 3. The tendency of the aldehydes to form trimers is well known.

Values for K_2, the distribution constant for single molecules, and for K_3, the association constant in the non-aqueous phase, may be calculated. K_2 may be taken equal to K_i, the intercept of the experimental equation. K_3 may be found by taking the quantity, $2K_3K_2^2$, equal to the experimental slope, K_s, and solving. In this way have been obtained the values for K_2 and K_3 given in table 1. Hendrixson (3) has calculated some similar constants for benzoic acid, and Smith and White (2) have calculated constants for a number of organic acids by other methods. The distribution constants obtained in the above manner from the data of Smith and White on propionic and isobutyric acid are practically equal to the constants calcu-

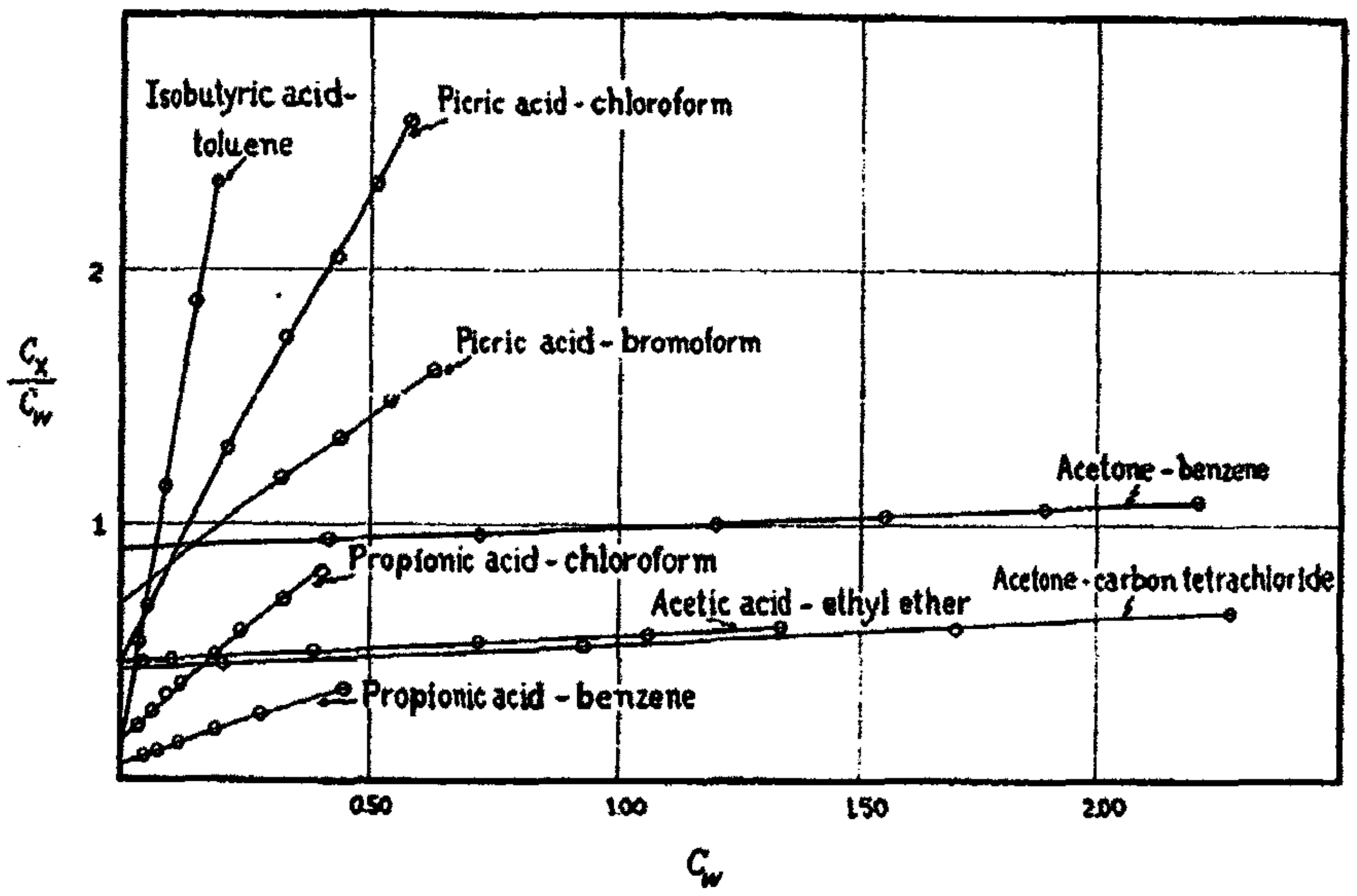

FIG. 1. THE RELATION OF THE APPARENT DISTRIBUTION RATIO, C_x / C_w, TO THE CONCENTRATION IN WATER, C_w, OF A NUMBER OF ASSOCIATING SUBSTANCES DISTRIBUTED BETWEEN WATER AND OTHER SOLVENTS AS INDICATED, AT 25°C.

TABLE 1

Distribution and association constants calculated from partition data at 25°C.

DISTRIBUTED SUBSTANCE	NON-AQUEOUS SOLVENT	DISTRIBUTION CONSTANT K_1	ASSOCIATION CONSTANT K_2
Acetic acid	Benzene	0.0106	108
	Chloroform	0.065	4.1
	Ethyl ether	0.46	0.24
Acetone	Carbon tetrachloride	0.43	0.28
	Benzene	0.91	0.050
Picric acid	Chloroform	0.46	8.6
	Bromoform	0.68	1.6
Lactic acid	Ethyl ether	0.081	0.97
Isobutyric acid	Toluene	0.138	281
	Benzene	0.180	201
	Chloroform	0.56	54
Propionic acid	Toluene	0.046	134
	Benzene	0.063	78.5
	Chloroform	0.164	30.0

lated by these authors. Their association constants are in error throughout by a factor of 2, but otherwise agree well with the reciprocal of K_3.

The simple equation is valid over what may be considered a significant and useful range of concentrations. A multitude of factors, however, may cause a departure from the equation. At very low concentrations, certain classes of substances undergo electrolytic dissociation which becomes sufficient to cause a noticeable lowering of the ratio, C_x/C_w, but may be taken into account when the dissociation constants are known. At high concentrations, on the other hand, association in the aqueous phase must increase to an important extent, also exerting a lowering influence on the ratio.

The solvents are at all times saturated with each other. In addition, their mutual solubility increases with increasing concentrations of the dissolved substance until, in many cases, the system becomes a single phase. These effects greatly hinder a correlation of partition data with that secured from studies of freezing point lowering, partial pressures, etc., in unmixed solvents. Saturation of either phase with the distributed substance causes a failure of all partition laws.

In developing the equation for the apparent distribution ratio it was assumed that n is the same in both solvents. It cannot be proven, at present, that this is the case, or that only one value of n exists in any one solvent, or that for any one value of n the molecules associate always in the same way.

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SIMPLIFIED FORMULAS FOR THE CALCULATION OF EXPANSION COEFFICIENTS AND COMPRESSIBILITIES OF GASES AT LOW PRESSURES FROM THE BEATTIE-BRIDGEMAN EQUATION OF STATE

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J. A. Beattie and O. C. Bridgeman (1) have developed an equation of state that relates p, V, and T in a simple form involving only five constants, each set of constants being specific to a gas in addition to the gas constant R. The equation may be written in the virial form in terms of either p or V and is expressed:

$$p = \frac{nRT}{V} + \frac{n^2\beta}{V^2} + \frac{n^3\gamma}{V^3} + \frac{n^4\delta}{V^4} \tag{1}$$

where

$$\beta = RTB_0 - A_0 - Rc/T^2 \tag{2}$$

$$\gamma = -RTB_0b + A_0a - RB_0c/T^2 \tag{3}$$

$$\delta = RB_0bc/T^2 \tag{4}$$

A_0, a, B_0, b, and c are the characteristic constants for each gas.

From equation 1 Beattie (2) derives the value of V in terms of p and obtains:

$$V = \frac{nRT}{P} + \frac{n\beta}{RT} + \frac{n\gamma}{R^2T^2} \cdot p + \frac{n\delta}{R^3T^3} \cdot p^2 \tag{5}$$

It will be observed from an examination of the equations as written in the virial forms that the values of p or V at 0°C. and 100°C. may be calculated by insertion of the correct values of β, γ, δ, the values of these coefficients at the two temperatures stated being calculated from equations 2, 3, and 4.

Values of the five constants for thirteen gases have been conveniently tabulated (3) and from these values β_1 and γ_1 at 100°C. have been calculated, the values of the virial coefficients at 0°C. having been obtained from computations made by Beattie and Bridgeman.

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From a knowledge of these values it is possible to calculate the coefficients of expansion at constant pressure (α_v) and constant volume (α_p), for

$$\alpha_v = \frac{1}{v_0}\left[\frac{dv}{dt}\right]_{p\,=\,\text{const.}}$$

$$\alpha_p = \frac{1}{p_0}\left[\frac{dp}{dt}\right]_{v\,=\,\text{const.}}$$

where v_0, p_0 represent the volume or pressure of the gas at 0°C. and $\frac{dv}{dt}$, $\frac{dp}{dt}$ the rate of increase of volume or pressure with temperature.

The values of α_v, α_p, here derived are for the temperature interval 0°C. to 100°C. and at a constant pressure of 1 atmosphere in the first case and an initial pressure of 1 atmosphere in the second case.

If we consider 1 gram-molecule of gas (that is, $n = 1$) then we have from equation 1

$$p_0 = \frac{RT_0}{V} + \frac{\beta_0}{V^2} + \frac{\gamma_0}{V^3} \quad \text{at } 0°\text{C.}$$

$$p_1 = \frac{RT_1}{V} + \frac{\beta_1}{V^2} + \frac{\gamma_1}{V^3} \quad \text{at } t°\text{C.}$$

and from equation 5 when the pressure is 1 atmosphere we have:

$$V_0 = RT_0 + \frac{\beta_0}{RT_0} + \frac{\gamma_0}{R^2T_0^3} \quad \text{at } 0°\text{C.}$$

$$V_1 = RT_1 + \frac{\beta_1}{RT_1} + \frac{\gamma_1}{R^2T_1^3} \quad \text{at } t°\text{C.}$$

Taking as our units those cited by Beattie and Bridgeman, i.e., moles, liters, atmospheres and ° Kelvin, we may calculate values of α_v at a constant pressure of 1 atmosphere and α_p at an initial pressure of 1 atmosphere over the range 0°C. to 100°C. from the following equations:

$$\alpha_v = \frac{\left[RT_1 + \frac{\beta_1}{RT_1} + \frac{\gamma_1}{R^2T_1^2}\right] - \left[RT_0 + \frac{\beta_0}{RT_0} + \frac{\gamma_0}{R^2T_0^2}\right]}{\left[RT_0 + \frac{\beta_0}{RT_0} + \frac{\gamma_0}{R^2T_0^2}\right] \cdot 100}$$

where $p = 1$ atmosphere, $T_0 = 273.13$°C., $T_1 = 373.13$°C., and

$$\alpha_p = \frac{\left[RT_1 + \frac{\beta_1}{V} + \frac{\gamma_1}{V^2}\right] - \left[RT_0 + \frac{\beta_0}{V} + \frac{\gamma_0}{V^2}\right]}{\left[RT_0 + \frac{\beta_0}{V} + \frac{\gamma_0}{V^2}\right] \cdot 100}$$

where V = const. = 22.4131 liters at N.T.P.

Substituting values of β which contribute the major portion to the divergence from the perfect gas law, and values of γ which contribute about 1 in 15,000 as a maximum to the value of the coefficient, we arrive at the values given in table 1, which are compared with those calculated by Leduc (4) and those determined experimentally. The experimental figures have been taken from the International Critical Tables, and where necessary the values at 1 atmosphere have been interpolated from the data given. Values not obtained from the International Critical Tables have a definite reference given.

It may be claimed that the performance of the equation is extremely good: it shows clearly the phenomenon that α_p for hydrogen, nitrogen, and helium is greater than α_v. The values for nitrogen, oxygen, and air are certainly reliable and that for carbon dioxide agrees well with the predictions of Leduc and the experimental figure. The values for methane are a little unsatisfactory and those for ethylene are disappointingly low compared with the calculations of Leduc; investigation into this point seems desirable. For ammonia the predictions are satisfactory in the case of the pressure coefficient, the value calculated agreeing almost exactly with that experimentally observed, but it seems curious that the value of α_v shows such a discrepancy. It would appear that values of the volume coefficient are more susceptible to external factors, such as the increase in volume caused by the evolution of adsorbed layers from the surface of the

TABLE 1

GAS	COEFFICIENTS* AT CONSTANT PRESSURE			COEFFICIENTS AT CONSTANT VOLUME		
	α_v (calculated)	Leduc (calculated)	Experimental	α_p (calculated)	Leduc (calculated)	Experimental
He	3659.1	—	3659	3661.3	—	3661
Ne	3660.6	—	3660[5]	3662.8	—	3661[5]
A	3672.4	—	3673	3671.7	—	3672
H_2	3660.3	3662	3660	3662.7	3664	3662
N_2	3670.9	3671	3670.5	3671.8	3672	3671.5
O_2	3674.6	3673	3674	3673.5	3672	3674
Air	3671.1	—	3671	3671.6	—	3672
CO_2	3721.7	3723	3723	3710.0	3712	3712
CH_4	3689.4	3681	3683	3688.1	3678	3680
C_2H_4	3724.2	3735	—	3710.5	3722	—
NH_3	3790.0	380	3847[6]	3767.8	377	3769[6]
CO	3670.9	3672	3669[7]	3671.8	3673	3668[7]
N_2O	3721.7	3732	3720[7]	3710.0	3719	—

* All these coefficients have been multiplied by 10^6 except Leduc's figures for ammonia, which are multiplied by 10^5.

containing vessels with rise in temperature and thereby vitiating the true values of the increase of volume with temperature.

The values for carbon monoxide and nitrous oxide are assumed by Beattie and Bridgeman (8) to be the same as those for nitrogen and carbon dioxide. This assumption seems fully justified in the case of carbon monoxide, but for nitrous oxide this is probably not quite true, as shown by the divergence between the predicted values of Leduc and those calculated from the Beattie constants for carbon dioxide.

The compressibility of a gas is given by the equation

$$1 + \lambda = \frac{p_0 v_0}{p_1 v_1}$$

at constant temperature, where p_0v_0 is the product at zero pressure and p_1v_1 the product at 1 atmosphere.

From the Beattie-Bridgeman equation of state we have at any temperature, T_1,

$$(1 + \lambda)_{T_1} = \frac{RT_1}{RT_1\left(1 + \frac{\beta_1}{RT_1V_1}\right)}$$

for

$$p_1V_1 = RT_1 + \frac{\beta_1}{V_1}$$

where V_1 is the corresponding volume of 1 gram-molecule at T_1° Absolute and β_1 is of the appropriate value. The omission of the further terms in the Beattie equation is justifiable at low pressures in this case, as values of $\frac{\gamma_1}{V^2}$ only contribute about 1 part in 100,000 to the final result.

As

$$V_1 = RT_1 + \frac{\beta_1}{RT_1} \text{ (approximately)}$$

then

$$(1 + \lambda)_{T_1} = 1 - \frac{\beta_1}{RT_1\left[RT_1 + \frac{\beta}{RT_1}\right]} = 1 - \frac{\beta_1}{R^2T_1^2 + \beta_1}$$

This simple form of equation allows the compressibilities of any gas to be calculated extremely rapidly over a wide temperature range, and in the case of the more compressible gases, such as carbon dioxide, the error involved is not greater than 1 part in 10,000. The agreement between the theoretical derivation of $1 + \lambda$ for temperatures between −100°C. and +100°C. and the experimental figures of Holburn and Otto (9) for nitrogen is satisfactory; and the assumption of Beattie and Bridgeman previously mentioned as regards the similarity of carbon monoxide and nitrogen seems fully borne out in the comparison of the values obtained from the data of Bartlett and his coworkers (10) on carbon monoxide and those calculated for nitrogen.

In table 2 the values $(1 + \lambda)_A$ are those calculated from the Beattie constants for nitrogen and those from Smith and Taylor's data (1) are given in the column designated $(1 + \lambda)_B$. $(1 + \lambda)_C$ values are the experimental determinations of Holborn and Otto for nitrogen, and the values given for $(1 + \lambda)_D$ are the figures obtained by Bartlett and coworkers for carbon monoxide.

TABLE 2

t°C.	$(1 + \lambda)_A$	$(1 + \lambda)_B$	$(1 + \lambda)_C$	$(1 + \lambda)_D$
−100	1.00369	—	1.00367	—
−50	1.00146	—	1.00144	1.00135
−25	1.00090	1.00082	—	1.00077
0	1.00051	1.00047	1.00046	1.00040
+25	1.00025	1.00024	1.00020	1.00018
+50	1.00006	1.00006	1.00000	1.00008
+100	0.99979	—	0.99980	0.99978

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SOME EXPERIMENTS WITH WETTING AGENTS

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The surface activities of members of the homologous series of aliphatic acids and their sodium salts have been reported by various investigators (1). These substances show, in general, increasing surface activity, or ability to lower the surface tension of water, with increase in length of the carbon chain in agreement with Traube's rule. The measurement of the surface activities of some sulfonates of the benzene series was undertaken to show the influence of the nature of the substituent alkyl group and of its position in the benzene nucleus in relation to the polar sulfonate group.

Recently new types of compounds in which the active or polar part of the molecule is a sulfate or sulfonate group have been developed commercially and widely recommended as ideal detergents, wetting and penetrating agents. The stability of solutions of these compounds in the presence of acids and in hard water permits their application under conditions which would prohibit the use of soap. The uses, advantages, and method of manufacture of one class of these products, the "sulfonated" higher alcohols, have been discussed by Killefer (2). Our experiments were extended to measure the adsorption or rate of exhaustion of such compounds from their water solutions by wool, and to study their effect when used as leveling agents in dyeing.

I. PREPARATION OF SULFONATES AND SURFACE TENSION MEASUREMENTS

The sulfonation of benzene, toluene, xylene, and cymene was accomplished by the general method of Gatterman (3), using fuming sulfuric acid and the minimum temperature required for each reaction. The sodium sulfonate was precipitated by treating the reaction products with saturated sodium chloride solution, or was obtained by neutralization with sodium hydroxide and evaporation. The sodium sulfonate was then purified by recrystallization from absolute alcohol or acetone until it was free of sulfate. Acetone was the more effective medium for the purification of the higher members of the series. Ethylbenzene, isopropylbenzene

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and butylbenzene were prepared by the Fittig synthesis (4), were then sulfonated, and their sodium salts obtained and purified as described above.

Solutions of these salts in distilled water were prepared and their surface tensions were measured over a range of concentrations at a constant temperature of 18°C. These measurements were made by means of an improved torsion balance which was fully described by De Gray (5) in a recent article. The static or equilibrium surface tension values for these solutions are shown in figure 1.

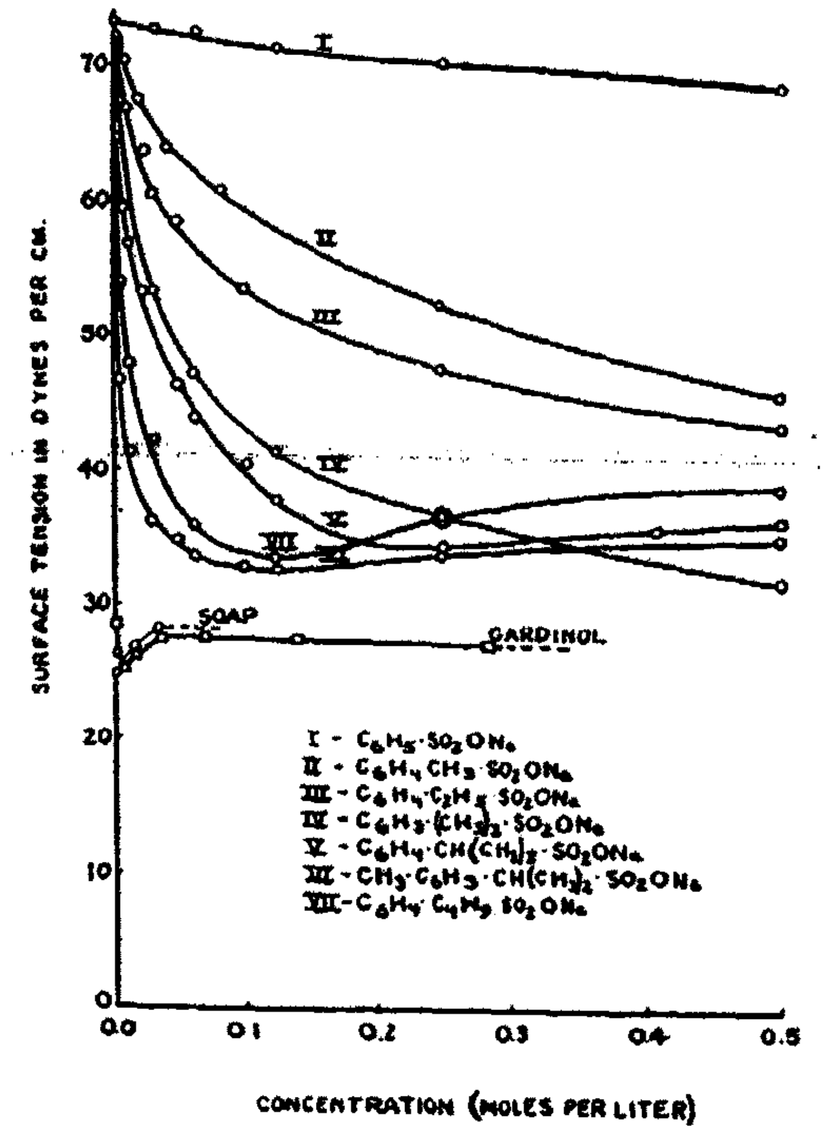

FIG. 1. LOWERING OF SURFACE TENSION BY SULFONATES OF BENZENE SERIES

In the case of sodium benzenesulfonate the observed lowering of the surface tension of water is roughly proportional to the concentration of the solute. In this its effect is similar to that of the lower members of the aliphatic series of acids or their salts and, in general, of substances in true solution which decrease surface tension. Beyond this first member the curves show increasing tendency to sag or to deviate from the straight-line relationship as the alkyl substituents increase in length or complexity. It is of interest to note that although the sulfonates of ethylbenzene (curve III) and xylene (curve IV) are identical in molecular weight, the latter is considerably more effective in lowering the surface tension of water.

This indicates that two substituent groups increase the surface activity of the compound more than a single group containing the same total number of carbon atoms. This point is exemplified further in the curves for the sulfonates of butylbenzene (curve VII) and cymene or *p*-methylisopropylbenzene (curve VII). These two curves also exhibit a minimum which is a characteristic of active surface-tension depressants and usually indicates a colloidal condition of the solute. With the exception of sodium benzenesulfonate, the solutes represented by the curves in figure 1 are probably mixtures of isomers.

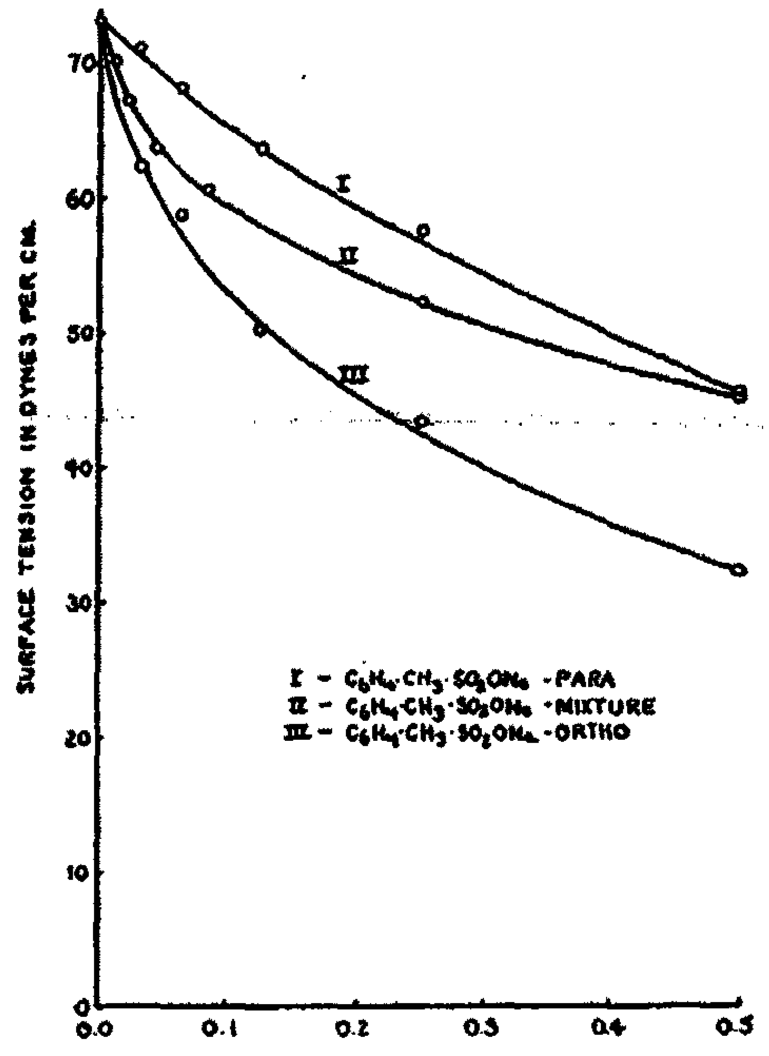

FIG. 2. COMPARISON OF *o*- AND *p*-TOLUENESULFONATES

In the sulfonation of toluene a mixture of two isomers is obtained. This mixture is composed of approximately 70 per cent of the para and 30 per cent of the ortho isomer. These two isomers were separated by taking advantage of the different melting points of the corresponding toluenesulfonyl chlorides, according to the method recommended by Beilstein (6). The *o*-toluenesulfonate and *p*-toluenesulfonate obtained from the separated sulfonyl chlorides were recrystallized from absolute alcohol, and surface tension measurements were made upon the solutions of each. These results are shown in figure 2 in relation to the curve for the mixture of the two isomers. It will be observed that the ortho derivative is more effective than the para as a surface tension depressant and that in low concentrations the activity of the ortho isomer predominates in the mixture, while in more concentrated solutions the surface activity of the mixture approaches that of the less active para component.

II. ADSORPTION OF WETTING AGENTS BY WOOL

For these experiments a fine grade of virgin wool was thoroughly degreased by scouring with soap and sodium carbonate, rinsed with distilled water and air dried. It was kept at constant humidity to attain a moisture content of approximately 13 per cent. Samples of wool weighing 5 g. were soaked for one hour at 50°C. in 500 cc. of the solutions of the wetting agents. The wetting agents used were the commercial products known as "Gardinol C.A." (compound A) and "Igepon T" (compound B). Both are sodium salts, the former a sulfate of a higher alcohol (2) and the latter a sulfonate of a condensation product. The solutions contained 0.5 per cent of the wetting agents and were made acid or alkaline by the addition of hydrochloric acid or sodium hydroxide. The pH values were determined colorimetrically at the end of the soak by means of standard indicators.

The percentage exhaustion of the wetting agent by adsorption was determined, after removing the wool, by evaporating 100-cc. portions of the solutions, drying the residue at 100°C. in an oven and weighing it. When hydrochloric acid or sodium hydroxide had been used to change the pH of the solution, this was carefully titrated and the weight of the salt formed was subtracted from the weight of the residue. This weight was also corrected for the weight of wool dissolved by the solution in each case. The actual proportion of wetting agent adsorbed by 5 g. of wool from 500 cc. of solution was obtained by comparing the corrected weight of the residue with the weight of residue resulting from 100 cc. of a solution of the wetting agent in which no wool had been soaked. The results, expressed as percentage exhaustion from solution, are represented in figure 3. Since the weight of wool used in each experiment was twice the weight of wetting agent present in the solution, the adsorption percentages based upon the weight of wool will be one-half the values represented by the curves in figure 3. For example, at pH 1.5 the solution of compound B is 22.9 per cent exhausted; under these conditions the wool has adsorbed 11.45 per cent by weight of this wetting agent. The experiments show that these substances are adsorbed from solution by wool in appreciable amounts only in acid solutions and that the amount of adsorption increases with increase in hydrogen-ion concentration.

These results can be interpreted by considering the nature of the compound in relation to the variation in the electrical charge of wool with change in pH. The wetting agents are sodium salts which, in water solution, produce surface-active anions containing a polar group and a long carbon chain. These negative ions are similar to the color ions of acid dyes and are similarly adsorbed by wool which bears a positive charge in acid solutions. The isoelectric point of wool, as reported by Harris (7), occurs at pH 3.4. Some adsorption of the wetting agent occurs beyond this point, just as the adsorption curves of acid and basic dyes overlap to some extent. However, as the acidity decreases beyond pH 3.4, the negative charge on the wool rapidly increases, and in this condition the wool repels the negatively charged ions so that no measurable adsorption occurs in this region. It is generally recognized that soap is not selectively adsorbed from its solution (pH 10–11) by textile fibers; the explanation of this fact is obvious, since the surface-active ion (or ionic micelle) of soap is likewise negatively charged.

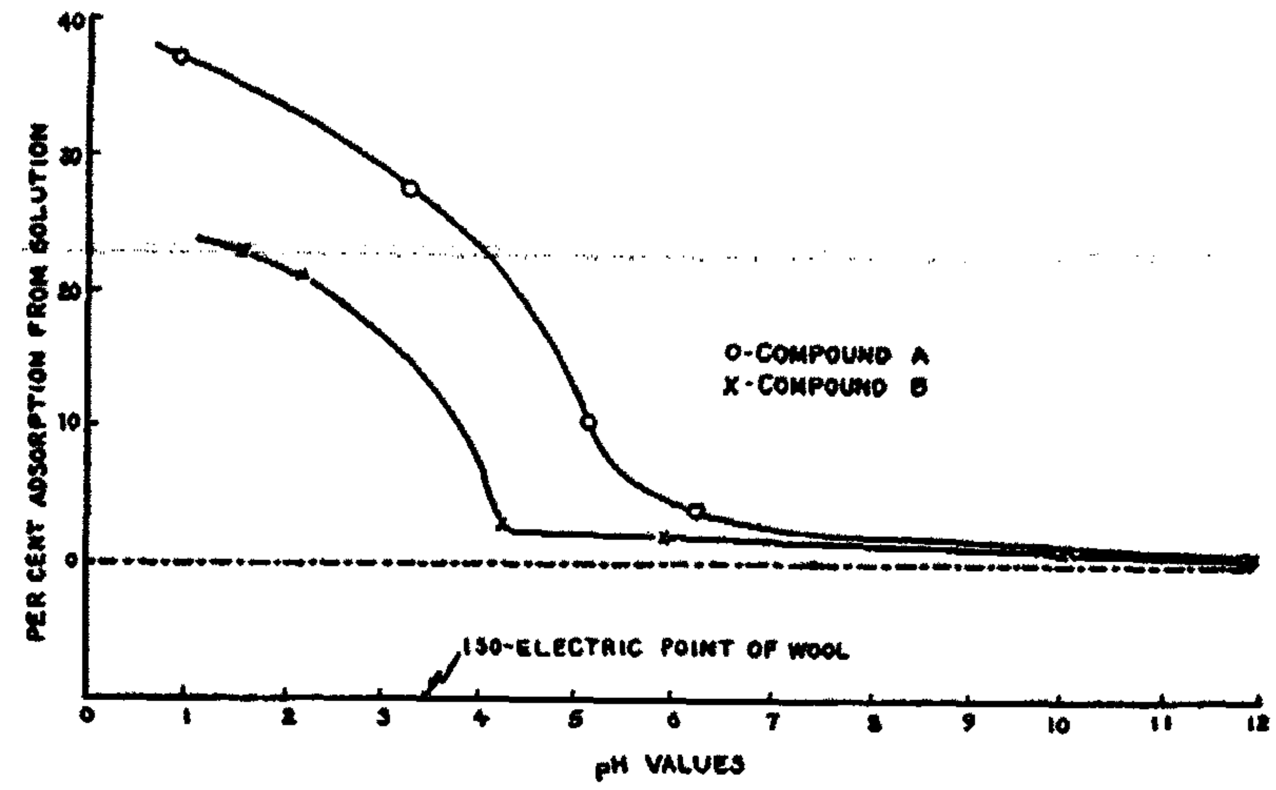

FIG. 3. THE ADSORPTION OF WETTING AGENTS BY WOOL

The practical conclusion to be drawn from these experiments is that, although they are stable in acid solutions, the new types of wetting agents are so strongly adsorbed from solutions of high acidity that they can hardly be employed economically under these conditions.

While no compounds furnishing positive ions of high surface activity were available for testing, it may be predicted that such substances would, like basic dyes, be strongly adsorbed by wool from alkaline solutions and negligibly adsorbed from acid solutions.

III. THE INFLUENCE OF WETTING AGENTS UPON THE ADSORPTION OF ACID AND BASIC DYES BY WOOL

The wool used for these experiments was a fine, white worsted knitting yarn. It was maintained at constant humidity, and one meter (about 0.5 g.) was accurately weighed for each test. Methylene blue was used as the basic dye at a concentration of 0.2 per cent; the acid dye was Orange II, and the concentration of the dye solution was 0.1 per cent in this case. Series of experiments with each dye were also performed in which Gardinol was added to the extent of 0.1 per cent and 0.5 per cent of the weight of the solution. The samples of wool were boiled for 2 minutes in 50-cc. portions of the dye solutions, which were made acid or alkaline with sulfuric acid or sodium carbonate respectively. Each sample of wool was transferred from the dye bath to distilled water and boiled for 2 minutes. It was then placed in an Erlenmeyer flask, covered with distilled water, and the air was displaced by carbon dioxide. The contents of the flask were heated to boiling and the dye on the wool was titrated with titanous chloride, using a slight excess of this reagent. The boiling was continued until the color was completely discharged and the excess of titanous chloride was then titrated with a solution of the same dye which served as its own indicator. A steady stream of carbon dioxide was passed through the flask throughout the titration. The pH values of the dye baths were obtained, after removing the wool, by means of a quinhydrone electrode.

The results for the acid dye are shown in figure 4 and for the basic dye in figure 5. The percentages are based upon the weight of the wool. Quantitative data for the adsorption of acid and basic dyes have been published by Briggs and Bull (8), who also studied the effect of the addition of salts to the dye bath. The results represented by curve I for each dye are consistent with the data of Briggs and Bull and with Bancroft's generalizations for the adsorption of dyes (9). With regard to the influence of the wetting agent or leveler, this can again be interpreted from a consideration of the nature of the surface-active ion in relation to the electrical condition of the wool. As shown in figure 3, Gardinol is strongly adsorbed by wool in acid solutions and, since its active ion is negative, this interferes with and decreases the adsorption of an acid dye in which the surface-active ion is also negative. In the case of the basic dye in which the active ion is positive, its adsorption is increased in acid solutions by Gardinol because of the strong adsorption of the negative ion of Gardinol. This is entirely consistent with Bancroft's statement that a readily adsorbed anion will increase the adsorption of a basic dye and decrease the adsorption of an acid dye. However, in alkaline solutions the adsorption of the basic dye is decreased by the Gardinol. This is apparently in contradiction to the rule just stated, but is not so in reality since, of course, an anion is not "readily adsorbed" by wool in an alkaline solution. The ability of Gardinol to decrease the adsorption of the basic dye in alkaline solutions may be attributed to its peptizing or detergent action, or its negative ion (or micelle) may be thought of as competing with the negatively charged wool for the dye cation.

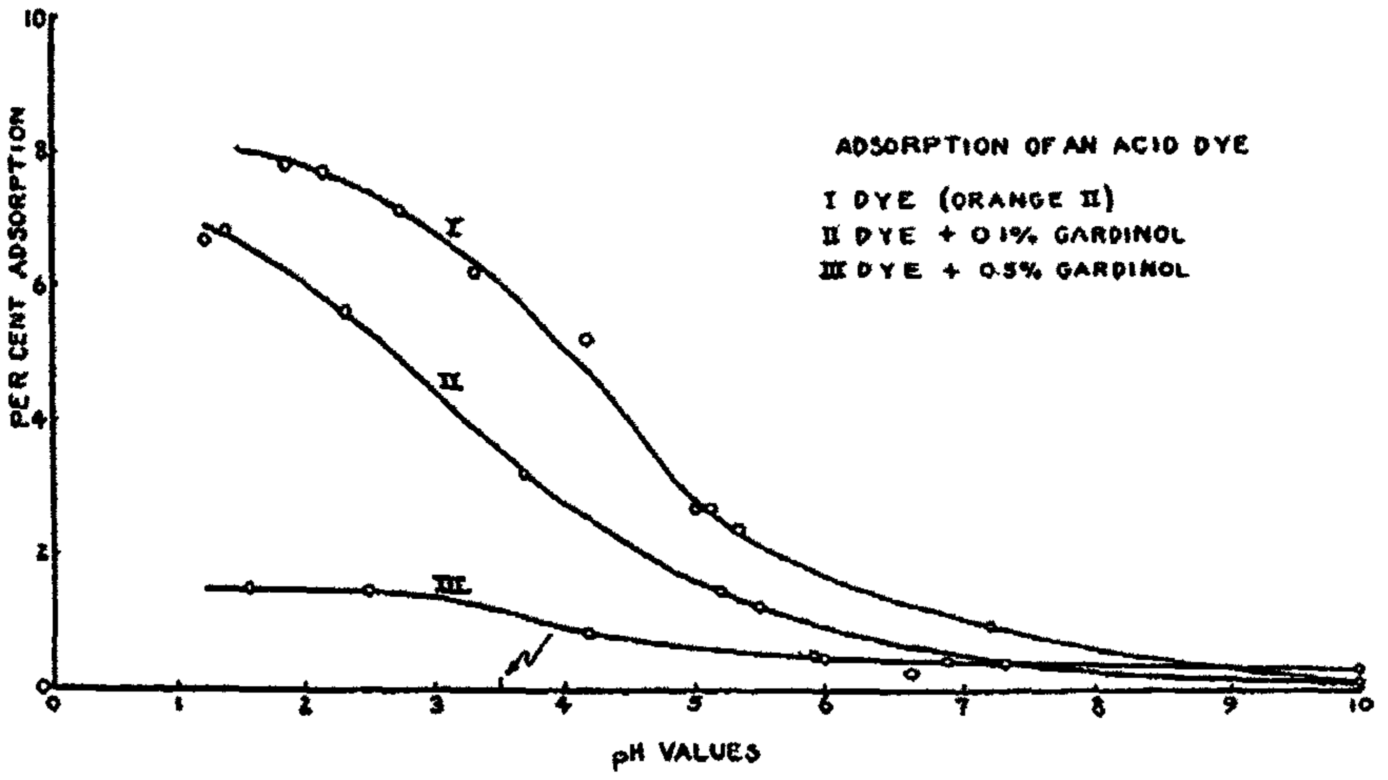

FIG. 4. THE INFLUENCE OF A LEVELING AGENT UPON THE ADSORPTION OF AN ACID DYE BY WOOL

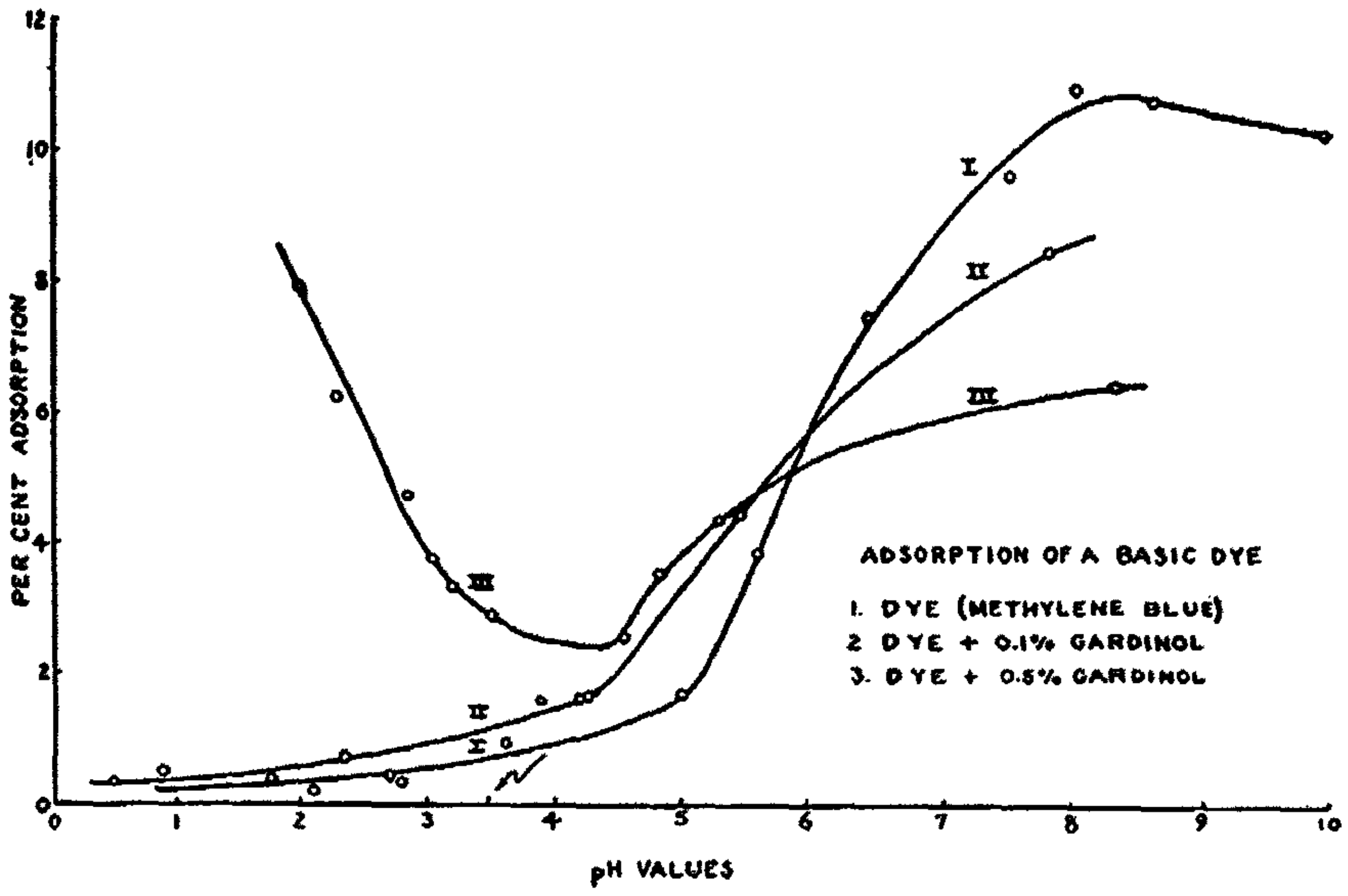

FIG. 5. THE INFLUENCE OF A LEVELING AGENT UPON THE ADSORPTION OF A BASIC DYE BY WOOL

SUMMARY

1. A number of the sulfonates of the benzene series have been prepared and the effect of the nature and position of substituent groups upon their surface activities has been studied. The surface tension–concentration relations of these products are compared with those of soap and other wetting agents.

2. The adsorption of some commercial wetting agents by wool has been measured in solutions having various hydrogen-ion concentrations. It is shown that, for substances of this type, the adsorption parallels the potential curve of the wool in acid solutions and is negligible in alkaline solutions.

3. The influence of wetting agents upon the take-up of acid and basic dyes by wool at various hydrogen-ion concentrations has been determined quantitatively. These agents increase the take-up of basic dyes in acid solutions and decrease dyeing under other conditions. The results are interpreted in terms of the electrical condition of the fiber and the adsorption of the surface-active ions.

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THE MECHANISM OF THE FORMATION OF KOHLSCHÜTTER'S SILVER SOL

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The colloidal dispersion commonly referred to as Kohlschütter's silver sol (1) is prepared by conducting a stream of hydrogen into a solution of silver oxide containing an excess of the solid oxide and maintained at a temperature of 50–60°C. Kohlschütter believed that the reduction took place on the walls of the vessel, both because the color of the sol varied with the nature of the vessel, and because in glass vessels of a given kind the velocity of the reduction was apparently directly proportional to the surface of the vessel exposed to the solution and inversely proportional to the volume of the solution. Thus in Thüringen soft glass and in quartz the sols were usually yellow-brown in color, and in Jena glass they varied from red through reddish-brown to violet and blue. In every case sol formation was accompanied by the deposition of a heavy black "mirror" of metallic silver on the vessel walls. The solubility of the glass was not regarded as an important factor in determining the nature of the sol, since the color of a sol formed in a certain kind of glass was the same even though the silver oxide solution used had been previously allowed to stand for a considerable time at 60°C. in another kind of glass.

Kohlschütter found that relatively large amounts of unreduced silver oxide remained in a sol even after prolonged treatment with hydrogen. The excess oxide may be removed by passing hydrogen through the sol contained in a platinized platinum vessel protected from the air with a bell jar. By this procedure the excess oxide was reduced, the silver depositing on the platinum vessel. The conductivity of the sols was reduced to 4 to 8 $\times 10^{-6}$ mhos, which was approximately one-tenth that of the original sols without any appreciable change in their appearance. On analysis he found, however, that the amount of silver in the colloidal particles had decreased during the purification process, and from this he deduced that the colloidal particles in the original sol contained some oxide. Since in general the particles in the yellow-brown sols contained more oxide than the particles in the reddish to blue sols, Kohlschütter claimed that the walls of the containing vessel determine the ratio of silver to silver oxide in a sol, as well as its color.

Erlach and Pauli (2) observed that a sol prepared by Kohlschütter's method, using hydrogen from a Kipp generator, always contained sulfur which came from hydrogen sulfide present in the hydrogen. Starting with pure silver oxide and pure electrolytic hydrogen there was said to be no sol formation in a hard glass or a silver vessel, but if a trace of potassium carbonate, sodium hydroxide, or ammonium hydroxide was added to the silver oxide solution a stable sol resulted. As a matter of fact, sols were obtained with electrolytic hydrogen, formed by electrolysis of sodium hydroxide, unless the gas was washed with concentrated sulfuric acid which was supposed to take out "alkali mist." The effect of alkali was attributed to the formation of an argentate, such as NaAgO, which served as the stabilizing electrolyte for the sol. In support of this they confirmed Kohlschütter's observations that the colloidal particles contained up to 20 per cent of unreduced silver. The stabilizing effect of a trace of hydrogen sulfide was attributed to the formation of some silver complex, but it is not obvious what this would be or how it would form.

Pauli's explanation of the necessity for sol formation of having either alkali or hydrogen sulfide in the reduction mixture is open to question. Pauli was unable to prepare a sol with pure silver oxide and pure hydrogen, but he was also unable to prepare a stable sol by the Bredig method in pure water. Best and Cox (3) had no difficulty with the latter preparation when they hit upon the right conditions and it seemed probable that a sol would result with pure hydrogen and silver oxide if one knew how to do it. As a matter of fact, the experiments to follow will disclose that silver sol formation by Kohlschütter's method is not determined either by the catalytic effect of the walls of the containing vessel, as stated by Kohlschütter, or by the presence of a substance capable of forming a complex negative stabilizing ion, as assumed by Erlach and Pauli.

EXPERIMENTAL

Procedure and reagents

The experimental procedure consisted simply in conducting hydrogen into silver oxide solutions in different kinds of glass vessels at a temperature ranging from 50–60°C. and noting what took place. Special attention was taken in the preparation and handling of the reagents. The silver oxide was precipitated from $N/10$ silver nitrate with a slight excess of $N/10$ sodium hydroxide, and washed ten times by decantation with boiling distilled water. A saturated solution was prepared by continuous shaking of a large excess of the solid oxide with 250 cc. of water for three to four hours. The entire process was carried out in the dark and the solutions were stored in the dark. Conductivity water from block tin stills was used throughout. The hydrogen was prepared by the process of Cooke and Richards (4).

The generator which contains the system, zinc amalgam–dilute hydrochloric acid–platinum, has been found to give hydrogen whose only impurity is a small amount of gaseous hydrogen chloride. To remove the latter the gas was passed over solid potassium hydroxide, then washed through distilled water and, as a final check on its purity, it was passed through a wash-bottle containing silver oxide solution before being conducted into the silver oxide solution in the reduction vessel.

The reduction vessels were test tubes with a hydrogen inlet tube of the same material. This type of vessel was chosen since it required the use of less of the pure reagents and assured thorough mixing and more intimate contact between the reacting compounds and the vessel walls. All connections in the gas train were glass to glass with one exception. Since a quartz reduction vessel and inlet tube was employed in some cases, the end of the quartz inlet tube was held against the end of the glass tube from the wash train by a short piece of gum rubber tubing which had previously been cleaned in a boiling sodium hydroxide solution and soaked in melted paraffin in a vacuum so that as the pressure was released into the evacuated space, the pores of the rubber were filled with the paraffin. This treatment of rubber has been found quite satisfactory in microanalytical work to prevent the rubber from giving off organic vapors and hydrogen sulfide. The same method of connection was used for all types of inlet tubes, for the sake of uniformity of procedure.

The reduction mixture was kept at the desired temperature by immersing in a water bath consisting of a 1-liter beaker of water heated by the flame from a microburner. The temperature was readily maintained within the desired limits and observations were easily made. A few drops of paraffin oil on the surface of the water decreased evaporation and this facilitated the maintenance of a constant temperature for long intervals.

Between runs the reduction vessels and the hydrogen inlet tubes were thoroughly cleaned as follows: The vessels were (1) soaked in concentrated nitric acid for six to twelve hours, (2) boiled with concentrated nitric acid for 5 minutes, (3) washed with distilled water and soaked for twelve to fifteen hours in several changes of distilled water, and (4) steamed for 5 minutes just before using.

Reduction of saturated silver oxide in the presence of excess solid

In order to test the effect of the containing vessel on the nature of the sol, mirror formation, and the action on solid silver oxide, observations were made with vessels of soft glass, Pyrex, and quartz. The results are summarized in table 1.

At the end of each of the above experiments the excess solid silver oxide was collected and, after washing several times with distilled water, it was found to be only partially soluble in dilute nitric acid (0.01 N) and in aqueous ammonia. The residues were washed and found to dissolve in concentrated nitric acid. From this it is apparent that the solid particles were partially reduced to metallic silver, the process being retarded gradually as the surface became coated with a silver film. Kohlschütter's statement that the solid silver oxide was not acted upon is obviously not in accord with the facts.

Although the differences in the colors of the sols were quite apparent, they were not as marked as would have been expected from Kohlschütter's report.

TABLE 1

Reduction of saturated silver oxide solution containing an excess of solid silver oxide

Temperature 55–58°C.

REDUCTION VESSEL	OBSERVATIONS		
	After a few minutes	After 3 to 4 hours	After 12 hours
Soft glass	Weak sol; silver mirror on walls.	Sol light yellow-brown in (T)[*] and yellow in (R)[†]. Deposit on wall increasing.	Dense sol, deep yellow-brown in (T) and dark gray to brown-green in (R). Heavy black mirror on walls of inlet tube and containing vessel.
Pyrex	Weak sol; silver mirror on walls.	Sol light yellow-brown in (T) and grayish yellow-green in (R). Deposit on walls increasing.	Dense sol, deep brown with a reddish tinge in (T) and grayish yellow-green in (R). Heavy black mirror on walls.
Quartz	Weak sol; no mirror.	Sol yellow-brown in (T) and yellow-green in (R); no mirror.	Dense sol, deep yellow-brown in (T) and dark brownish-green in (R); no mirror.

[*] (T) = transmitted light.

[†] (R) = reflected light.

Reduction of silver oxide solution in the absence of excess solid

Since solid silver oxide is reduced by hydrogen at 55–60°C., observations were made of the effect on the sol formation process of eliminating the excess suspended solid. The results are given in table 2.

The above sols attained their maximum color after three to four hours, showing no perceptible darkening thereafter. The black mirror deposit likewise deepened very little after the first few hours. In every case the sols contained appreciable amounts of silver in solution even after prolonged treatment with hydrogen.

Reduction of ultrafiltered solutions of silver oxide

Since reduction of filtered silver oxide solutions with hydrogen gave only weak yellow sols in spite of the fact that they contained considerable unreduced silver in solution, it seemed probable that the substance reduced was not the silver in solution but colloidally dispersed silver oxide that was not removed by filtration through an ordinary filter. In support of this it was found that the saturated solutions, such as used in the preceding experiments, always contained appreciable amounts of colloidally dispersed oxide. To remove this in so far as possible, the saturated solution was ultrafiltered before use. For this purpose a filtering membrane was prepared by impregnating No. 40 Whatman filter paper with collodion from a 4 per cent solution in glacial acetic acid. The membrane was used in a gold-plated ultrafilter in which the wire gauze usually employed was replaced with a sheet of perforated gold foil. At a pressure of 40 lbs. per square inch, 125 cc. of solution was filtered in 5 minutes. Filtration with a cellophane membrane was unsatisfactory, since it reduced the silver solution completely. The observations with ultrafiltered solutions in various vessels are given in table 3.

TABLE 2

Reduction of filtered saturated silver oxide solution

Temperature 55–58°C.

REDUCTION VESSEL	OBSERVATIONS		
	After 1 hour	After 5 to 6 hours	After 12 hours
Soft glass	Very weak sol; thin silver mirror on walls.	Light yellow sol; some darkening of mirror.	Almost the same as after 5 to 6 hours
Pyrex	Very weak sol; thin silver mirror.	Light yellow sol; some darkening of mirror.	Almost the same as after 5 to 6 hours
Quartz	Extremely weak sol; no mirror.	Light yellow-brown sol; no mirror.	Almost the same as after 5 to 6 hours

TABLE 3

Reduction of ultrafiltered solutions of silver oxide

REDUCTION VESSEL	OBSERVATIONS
Soft glass	Silver mirror starts to form after 1 hour and darkens gradually; little or no sol formation in 35 hours; silver ion in the solution.
Pyrex	Silver mirror starts to form after 1 to 2 hours and darkens slowly; no sol formation in 35 hours; silver ion in the solution.
Quartz	No sol formation and no mirror formation even after 100 hours; nephelometric analysis shows no loss in silver ion concentration.
Platinum (quartz + platinum foil)	No sol formation; no deposit on quartz tube; after 12 hours all the silver deposited on the platinum foil in the form of minute hexagonal platelets.
Silver (quartz + silver foil)	No sol formation or deposition of silver on either the walls of the quartz vessel or the silver foil.

The results shown in table 3 furnish conclusive evidence that silver oxide in true solution is not reduced in a quartz or silver vessel by hydrogen. Since there is no action in a quartz container, silver or platinum foil in a quartz vessel is equivalent to a container of the metal in question.

The reduction of dissolved silver oxide in the presence of platinum is due to catalytic activation of the hydrogen at the surface of the metal. As a result, hydrogen goes into solution as hydrogen ion and an equivalent amount of silver ion leaves the solution, giving a minute nuclear deposit of silver at certain points on the platinum surface. As the process continues, these nuclear deposits grow to relatively large hexagonal platelets of silver. This phenomenon does not take place at a silver surface because hydrogen is not catalytically activated to any appreciable extent by silver, under the conditions of the experiment.

The ease with which solid silver oxide, in suspension or on the walls of the vessel, is reduced by hydrogen indicates that hydrogen is activated at the surface of silver oxide or at the interface silver–silver oxide (5).

The reduction at the surface of the glass vessels with the formation of a mirror-like deposit is probably preceded by the formation of a film of silver oxide, which is subsequently reduced. The deposition of a silver oxide film is due either to adsorption from solution or to precipitation by means of alkali dissolved from the glass. In support of the latter view it has been found by H. L. Johnston[1] at Ohio State University, that the solubility of silver oxide in water, 2.2×10^{-4} equivalents per liter,[2] is reduced enormously by the presence of very small amounts of alkali. Thus 0.02 *N* alkali reduces the solubility to 6×10^{-6} equivalents per liter, which is approximately 3 per cent of the solubility in pure water. At a temperature of 50–60°C. sufficient alkali is extracted from the glass to cause the deposition of a film of oxide which is promptly reduced. Continuation of the process causes a gradual thickening of the mirror thus deposited. The process is in no sense a result of the catalytic activation of hydrogen by the glass surface. No film formation occurs on a quartz vessel because of the insolubility and non-alkaline character of the surface.

Further evidence in support of the above conclusions is furnished by the results of three experiments in which very dilute alkali, colloidal silver oxide and colloidal silver, respectively, are added to the ultrafiltered solution in a quartz vessel before conducting in the hydrogen. The silver oxide sol was formed by saturating and filtering a solution at 100°C. and cooling. The results are given in table 4. These observations support the view that

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[1] Private communications.

[2] Kohlschütter believed the solubility of silver oxide to be twice this value. The most probable explanation is that Noyes and Kohr (J. Am. Chem. Soc. **24**, 1143 (1902)) reported a value of 2.16×10^{-4} moles per liter, but their data shows that they meant to say 2.16×10^{-4} equivalents per liter.

sol formation and mirror formation by Kohlschütter's method result from reduction of solid silver oxide and not of the dissolved compound. Colloidal silver, like silver in mass, does not catalytically activate the hydrogen and effect reduction.

Because of the precipitation of silver oxide by the alkali extracted from glass, an ultrafiltered solution stored in a Pyrex flask for two weeks gave a light yellow sol on reduction in a quartz vessel. The precaution was therefore taken to store the stock solutions in quartz. The very slow formation of a weak sol in a glass vessel with the ultrafiltered solution may result from the breaking-off of pieces of the mirror first deposited on the walls, or of silver oxide itself before the latter is reduced.

TABLE 4

Reduction in a quartz vessel of ultrafiltered silver oxide solutions after certain additions

ADDITIONS	OBSERVATIONS
Solution made 2 to 5×10^{-4} to sodium hydroxide	Weak sol after 1 hour; light yellow to yellow-brown sol after 4 to 5 hours; no mirror; colorimetric examination shows that the depth of color increases with the sodium hydroxide concentration but not in direct proportion.
Colloidal silver oxide	Sols are formed, the depth of color of which was found by colorimetric analysis to be directly proportional to the amount of colloidal silver oxide added; no mirror formation.
Colloidal silver	No reduction of the solution and no mirror formation even after 30 to 40 hours.

Reduction of silver oxide solutions formed by diluting the saturated solution

In the experiments considered in the last section there is one possible source of error. In the ultrafiltration process to remove all silver oxide nuclei, the solution came in contact with both the ultrafiltration membrane and the rubber gasket. The possibility that some foreign substance was introduced which would inhibit the reduction process was not excluded. To get around this possible source of error, the colloidal silver oxide was removed from the saturated solution by diluting with enough water to dissolve the colloidal oxide. The dilutions were made in quartz vessels and the resulting solutions were allowed to stand for three to four days to establish equilibrium conditions. Some observations with such solutions are given in table 5.

It is apparent from the above experiments that a filtered saturated solution diluted in the ratio of 6 of solution to 4 of water is not reduced at all by hydrogen in a quartz vessel at 50–60°C. The solution diluted in the ratio of 7:3 showed barely perceptible sol formation. The obvious explanation is that the dilution in the ratio of 6:4 is sufficient to remove all colloidal oxide, thus eliminating reduction with the formation of silver sol. In soft glass at this dilution, mirror formation proceeds slowly and sol formation is extremely slow. The common ion effect of the alkali from the glass is localized at the surface, depositing a film of oxide which is subsequently reduced. If the dilution is in the ratio of 1:5, the alkali from the glass is insufficient to precipitate the oxide and no mirror formation results. This indicates that the precipitating action of alkali is a more important factor in the formation of a film of silver oxide on the glass than adsorption of silver oxide from solution by the glass wall. For if the latter were the important thing, one would expect some mirror formation from the diluted solution, especially since the adsorption is in general proportionately greater from more dilute solutions. The absence of mirror formation in quartz and silver with saturated solutions likewise indicates that the precipitating action of alkali from glass is more important than adsorption of silver oxide from solution, as the initial step in mirror formation.

TABLE 5

Reduction of silver oxide solutions formed by reducing saturated solutions

REDUCTION VESSEL	DILUTION Solution:water	OBSERVATIONS
Quartz	5:5	No sol and no mirror even after 30 to 40 hours.
Quartz	7:3	Very light yellow sol in 10 to 12 hours; no mirror.
Quartz	6:4	No sol and no mirror even after 30 to 40 hours.
Soft glass	6:4	Faint mirror after 2 hours, darkening gradually; very light yellow sol in 30 hours.
Soft glass	1:5	No sol and no mirror even after 30 hours.

Samples of solutions diluted in the ratio of 6:4, which are not reduced at all in quartz, were treated with alkali, colloidal silver oxide, and colloidal silver in the same way as the ultrafiltered solutions considered in the last section. The results were identical with those recorded in table 5 and are therefore not repeated here. These observations merely confirm the observations with ultrafiltered solutions and show that no complication was introduced by the ultrafiltration process.

In this connection it may be mentioned that the solubility of silver oxide determined by chemical methods is approximately 2.2×10^{-4}, while that by conductivity methods is 1.38×10^{-4} equivalents per liter (6). From this it is assumed that the silver hydroxide which is formed in solution is approximately 60 per cent dissociated. In view of the fact that 4 parts of water must be added to 6 parts of saturated silver oxide as ordinarily prepared in order to get rid of all colloidal silver oxide, it is suggested that the higher values of the solubility as determined by chemical methods may be due in part to the presence of some colloidally dispersed oxide in the solution. This question is now being investigated.

Effect of purity of the hydrogen on sol formation

It will be recalled that Pauli and Erlach failed to obtain silver sols in Pyrex vessels with pure solutions and electrolytic hydrogen freed from "alkali mist" with sulfuric acid. Since we always obtained sols with hydrogen, free from alkali, provided the saturated solution was not ultrafiltered or diluted to eliminate colloidal silver oxide, the failure of Pauli and Erlach to obtain sols must be explained on some basis other than purity of hydrogen. There are two possibilities: either the silver oxide solutions which they used were too dilute to give sols or mirrors with glass (see table 5), or the sulfuric acid used in the washing train to remove alkali mist substituted a sulfuric acid mist in its place. Since they doubtless worked with saturated solutions, the latter explanation appears the more probable. At any rate it was shown that a filtered saturated silver oxide solution which contained colloidal silver oxide gave no mirror or sol on treating with hydrogen for forty hours provided the solution was made 10^{-3} *N* with sulfuric acid. With 10^{-4} *N* acid very slight sol and mirror formation was observed after twelve hours. Sulfuric acid added directly or with the hydrogen has the same effect as dilution in removing silver oxide particles and in preventing the deposition of a silver oxide film on the walls of the vessel.

The results of this investigation may be summarized briefly as follows:

1. The formation of Kohlschütter's silver sol by the reduction of silver oxide with hydrogen at 50–60°C. is accomplished only in the presence of solid silver oxide. Saturated solutions that have not been ultrafiltered ordinarily contain appreciable amounts of the colloidally dispersed oxide.

2. In a quartz or silver vessel an ultrafiltered silver oxide solution undergoes no reduction with pure hydrogen at 50–60°C.; in a glass vessel the reduction is confined to the surface of the glass giving a thin mirror of metal; in a platinum vessel the reduction is at the surface of the metal, depositing relatively large hexagonal platelets of silver.

3. The reduction of silver oxide solution in a platinum vessel results from catalytic activation of the hydrogen at the platinum surface. There is no catalytic activation of hydrogen and no reduction at the surface of quartz or silver.

4. Mirror formation by reduction in glass vessels is not due to catalytic activation of hydrogen at the surface of glass as implied by Kohlschütter. The mirror formation is preceded by the deposition of a film of oxide which is subsequently reduced. The oxide film results chiefly from precipitation by means of alkali dissolved from the glass, but may be due in part to adsorption of the oxide from solution.

5. The ease with which solid silver oxide, in suspension or on the walls of the vessel, is reduced by hydrogen, indicates that hydrogen is readily activated at the surface of silver oxide or at the interface silver–silver oxide.

6. Pauli's view that sol formation will not take place except in the presence of alkali or sulfide which can furnish a complex stabilizing electrolyte, is not in accord with the experimental evidence herein recorded.

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NOTE ON THE POSSIBLE MAGNITUDE OF THE SORPTION ERROR IN MEASUREMENTS INVOLVING EASILY SORBABLE GASES AT LOW PRESSURES

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INTRODUCTION

Gases which are easily compressible condense readily as a rule on surfaces exposed to them. At sufficiently high pressures changes in the amount of gas condensed on the walls of an apparatus, resulting from alterations in the pressure, are small compared with changes in the quantity of gas contained in the free space of the apparatus. They may therefore be neglected, except in cases where a high degree of accuracy is required; for example, in measurements of gaseous densities for atomic weight determinations. Not so, however, at low pressures. Here, not only the amount of gas contained in the free space of the apparatus, but also the amount sorbed on the enclosing walls may vary directly with pressure—the so-called "Henry range." If the initial slope of the sorption isotherm is greater than that of the isochor for the apparatus concerned the two curves will intersect, for the latter continues to rise, whilst the former tails off more or less rapidly as saturation of the surface is approached. In such cases calculations based on the pressure changes observed in an apparatus of known volume may be subject to serious error, and this may escape unnoticed unless there is some possibility of controlling the results by an independent method.

The diagram of figure 1 represents a case in which the free gas content at 20°C. of an apparatus of two-liter capacity is compared with the early portion of a typical sorption[1] isotherm at the same temperature. In general there is no necessity for the two curves to intersect, as in the hypo-

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[1] In the absence of suitable data for glass the start of the 20°C. isotherm for sulfur dioxide on 0.05 g. of wood charcoal (writer's unpublished results) has been plotted. The smoothed curve is the commencement of a "Freundlich" equation, $A = 50.0\ p^{0.787}$, where A is given in micromoles and p in millimeters of mercury. An equation of the Langmuir type, $A = \frac{124\ p}{1 + 5.52\ p}$, would fit the upper points of the figure reasonably well, but falls however below the first three points.

thetical case depicted here. There will, however, usually be found a range of low pressure over which the slopes will not be widely different, and over this range the same remark applies.

APPARATUS

The apparatus in which the experiments about to be described were performed, was constructed for the purpose of examining the suitability

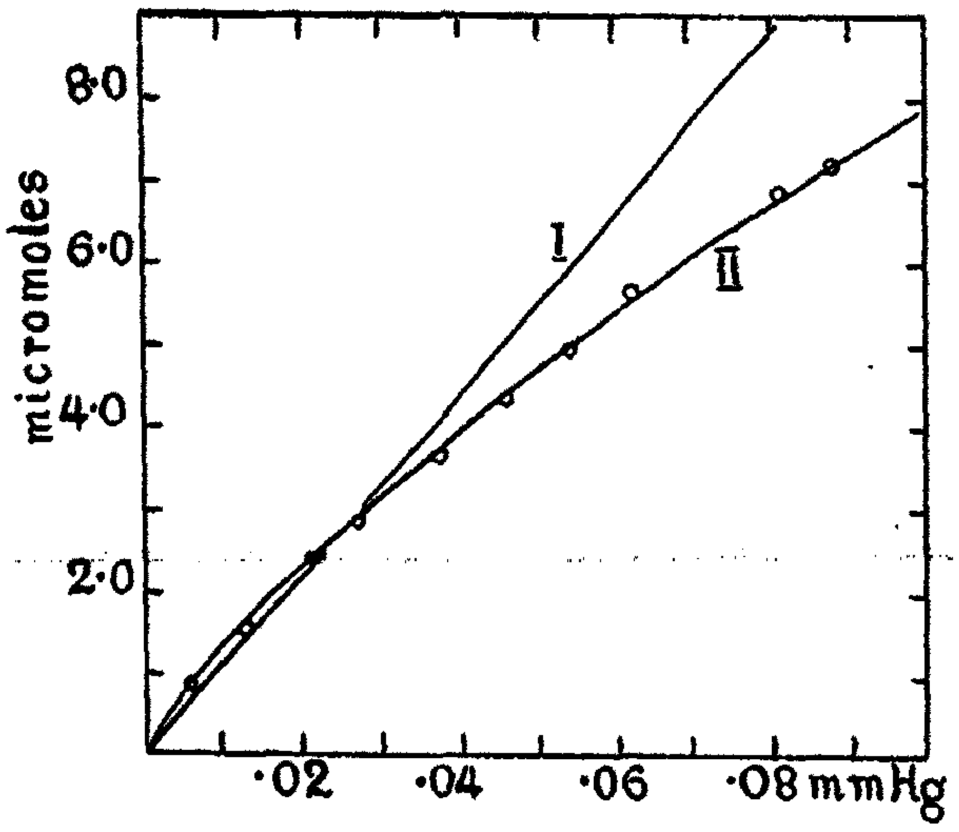

FIG. 1. *Curve I:* Isochor for apparatus of two-liter capacity at 20°C. May be considered a straight line for all gases over the pressure range here in question.

Curve II: Typical isotherm for easily condensible gas. Approaches a limiting saturation value at higher pressures unless capillary condensation intervenes.

of the McLeod gauge as an instrument for measuring low pressures of sulfur dioxide. In that section of the apparatus with which we are here concerned (figure 2), the following combinations were independently possible:—

$$\begin{tikzcd}
\text{Volume bulb} \arrow[r, leftrightarrow] \arrow[d, leftrightarrow] & \text{Gas train} \arrow[r, leftrightarrow] \arrow[d, leftrightarrow] \arrow[dl, leftrightarrow] & \text{Evacuating system} \arrow[d, dash] \\
\text{McLeod gauge No. 1} \arrow[r, leftrightarrow] & \text{McLeod gauge No. 2} \arrow[r, leftrightarrow] & \text{Gas supply}
\end{tikzcd}$$

The estimated surfaces and volumes of the different parts of the system bounded by taps or seals were as follows: gas train (T_1 to T_7), 750 sq. cm., 164 cc.; volume of bulb, R, 560 sq. cm., 997 cc.; McLeod gauge No. 1, G_1, 660 sq. cm., 319 cc.; McLeod gauge No. 2, G_2, 290 sq. cm., 269 cc. Volume estimates are probably more accurate than those of surface. The exact significance of estimates of the geometrical surface is uncertain, since calculations of sorption data based on such estimates in the case of glass indicate the existence of an unduly large number[2] of superposed layers of closely packed molecules under certain conditions.

The two McLeod gauges were similar in size and shape, each having a bulb of ca. 180 cc. volume and a compression chamber consisting of a length of quill tubing of cross section equivalent to 7.29 cu. mm. per millimeter, surmounted by a capillary of 1.88 cu. mm. per millimeter. At the highest mark a column of 1 cm. of mercury corresponded to a gas pressure of 1.5 microns of mercury in the system. The upper limit of the reading range of McLeod gauges was a pressure of 4 mm. of mercury.

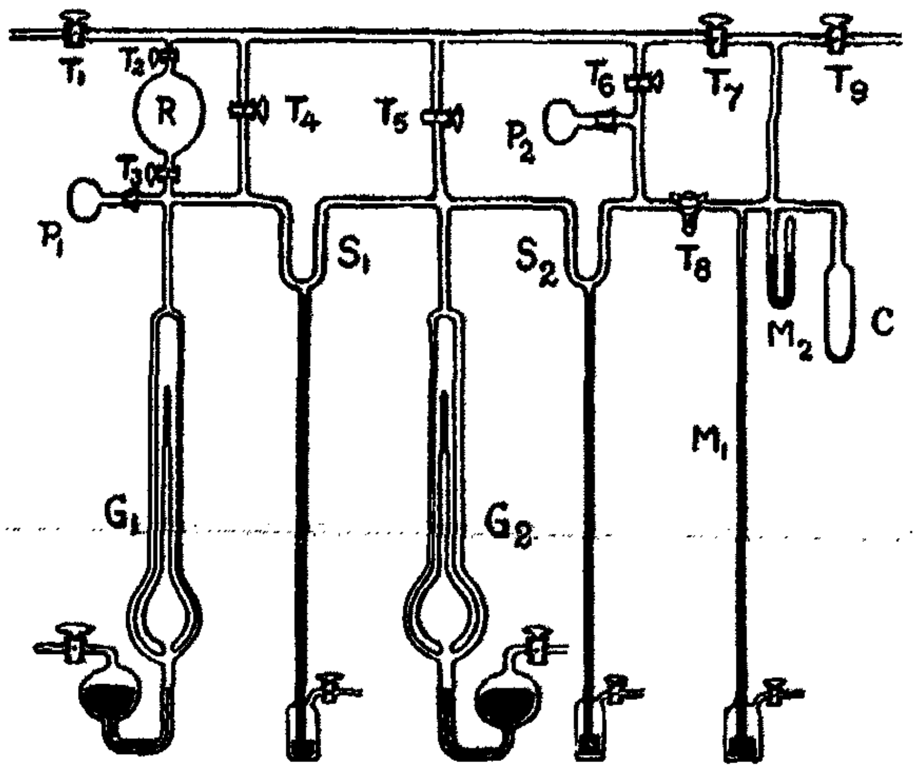

FIG. 2. APPARATUS USED IN THE EXPERIMENTS

R, volume bulb; G_1 and G_2, McLeod gauges; C, condensation bulb containing phosphorus pentoxide; P_1 and P_2, phosphorus pentoxide drying bulbs; M_1 and M_2, manometers for controlling pressure of gas to be admitted to micropipette; T_8, single-bore, three-way tap with appendix forming micropipette; T_1, tap to evacuating system; T_9, tap to reserve of sulfur dioxide.

Right-hand side of system:—McLeod G_2, bounded by mercury seals S_1 and S_2 and by tap T_5. Left-hand side of system:—McLeod G_1, bounded by S_1, T_3 and T_4, plus volume bulb R, plus gas train between T_1 and T_7.

The two gauges were connected directly by way of a mercury seal, S_1, but for the remaining connections carefully chosen glass taps lubricated with rubber grease (later replaced by Apiezon) were employed. Separating the system from the gas supply there was a capillary tap, T_8, with three outlets at 120° to one another but only one bore. One of the outlets had been sealed off to form a short appendix, and by connecting this with

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[2] For example, circa fifty layers of water, five layers of carbon dioxide (Langmuir: J. Am. Chem. Soc. 38, 2283 (1916)).

the source of supply and the system successively, the pressure in the latter could be increased by amounts as small as desired, the pressure of the supply having been suitably adjusted beforehand. This tap, the only one bounding the system to have on the other side sulfur dioxide at appreciable pressures, could be isolated by a second mercury seal, S_2, introduced between it and the McLeod gauge G_2.

TREATMENT OF APPARATUS

Following the usual practice, the constituent parts of the apparatus had been cleaned with chromic-sulfuric acid[3] mixture before assembly. After completion of the air calibration, for which one of the McLeod gauges served as reference volume, the apparatus was exhausted thoroughly and baked out at 250–300°C. with the mercury vapor pump running. Heating elements in the form of nichrome wire spirals wound on Pyrex quill and mounted parallel to the axes of sheet asbestos cylinders, reinforced where necessary by a backing of sheet "tin," were found very convenient for heating the gauges, which for this reason had been mounted on iron stands instead of the usual form of wooden support. In order to permit of their easy removal when not in use the heating ovens were hinged down one side. During the baking-out of the McLeod gauges the gas train and volume bulb were heated at intervals by the aid of the spirit flame. A cowl of asbestos sheet suitably arranged prevented the formation of a cold cap on the upper hemisphere of the volume bulb.

The outgassing treatment was repeated each time the gas in the apparatus was changed and whenever the accumulation of surface moisture was suspected, owing to the attainment of an apparently negative pressure on exhausting[4] or to a drop in the calculated pressures on passing from mark to mark on the McLeod gauge.

EXPERIMENTAL PROCEDURE

The experiment consisted in distributing a certain quantity of sulfur dioxide at low pressure between the different sections of the apparatus

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[3] This treatment, though customary in gas work, possesses the disadvantage of covering the surface of the glass with a layer of silica gel, thereby increasing the sorption characteristics of the apparatus (cf. H. S. Frank: J. Phys. Chem. 33, 970 (1929)). From this point of view swabbing out with cotton-wool soaked in benzene might be preferable, other things being equal, the solvent removing the grease and mechanical action the insoluble matter.

[4] Differences in the dryness of the surface of the glass in the compression chamber and its comparison capillary cause the depression of the mercury meniscus in the two to differ, although the diameters are the same in both (cf. L. Dunoyer: La Technique du Vide, p. 74). The effect was frequently observed after unusually high temperatures had prevailed in the laboratory for some hours at a time. Under such conditions there is a disengagement of water from lower sorption levels, which the pentoxide bulbs in the train are not able to remove immediately.

and measuring the pressure in each side independently. After each redistribution the apparent quantity of gas present in the apparatus was calculated from the known volumes of the different sections and the observed temperatures and pressures. The total quantity was then compared with an arbitrarily chosen initial reading for which the whole of the free gas had been collected in McLeod gauge No. 2, hereafter referred to as the right-hand side of the apparatus. When equality of pressure had been attained in both sides of the system, a further transfer of gas could be effected by applying a wad of cotton-wool soaked in liquid air to an appropriate section of the train for a short time and manipulating the taps accordingly. By proceeding in this manner it was possible to distribute the gas in either direction at will from a state of uniform pressure, or to collect practically the whole[5] of the free gas in either side of the system.

RESULTS

The results of a typical series[6] of distributions in both directions, repeated three times, are given in figure 3, in which the percentage variation from the initial reading has been plotted against the time in days from the start. In order to avoid undue extension of the time scale the intervals between the last readings on one day and the first on the next have been omitted. Lines joining the experimental points merely indicate the sequence of the readings; they do not, in general, represent an attempt at intrapolation.

In the course of the first distribution from right to left an apparent disappearance of gas was observed, sorption on the new surface exposed more than counterbalancing desorption from the old consequent upon the pressure drop in the right-hand side. Completion of the transfer was accompanied by a partial recovery of the loss. After returning the gas to the right-hand side of the system a gain of some 16 per cent (fifth day of figure 3) ensued, increasing to 20 per cent (eleventh day of figure 3) on repeating the cycle of operations. Sorbed gas was evidently being slowly disengaged from the enclosing walls of the system.

Since early experiments of Herbert[7] had already shown the impractica-

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[5] There was always a small after-release of gas on isolating a section of the apparatus which had been exposed to liquid air for a short period of time; hence the transfer of gas never appeared to be quite complete on attempting to collect the whole of the free gas in one side of the apparatus.

[6] In all, three series of distributions were performed with different quantities of gas in the system in each case. For reasons of economy in space the intermediate series only is discussed here; the preceding and following series, with twice and half as much free gas, respectively, in the system yielded entirely analogous results.

[7] J. M. B. Herbert (unpublished work performed at Manchester University). F. P. Burt (Trans. Faraday Soc. 130, 183 (1932)) reports that in the case of ammonia sorbed on glass several days exposure to the vacuum produced by charcoal cooled in liquid air is insufficient for the recovery of even half the quantity of gas sorbed during a week's run at atmospheric pressure.

bility of completely recovering sulfur dioxide sorbed on glass, even on raising the temperature, there did not appear to be any likelihood of success attending an effort at recovery from a system at room temperature. Accordingly no attempt was made to push the matter to a limit; instead, a condensation bulb in the system was immersed in liquid air for three periods of ten minutes or so and the whole of the condensed gas was then allowed to expand into (a) the whole, (b) the right-hand side, and (c) the left-hand side, respectively, of the system. The peaks on the thirteenth, fourteenth and fifteenth days of figure 3 represent the earliest points taken in each case.

It may be observed that the peak corresponding to the readings of the fourteenth day is double. This is due to the removal of a small quantity of permanent gas, which was found to have collected in the course of the experiments. It owed its origin in all probability to traces of air dissolved in the tap grease[8] during a check air calibration performed shortly before and now released under the combined influence of the low pressure in the apparatus and the high laboratory temperatures obtaining about this time on occasion. A correction based on the assumption of a uniform disengagement with time yields the dotted curve of figure 3; the general form of the curve is in no wise altered thereby and the effect is small compared with the other effects observed, so that a correction on this basis would appear to be not unjustified.

Examination of the curve of figure 3, particularly in the corrected form, indicates that, for all practical purposes, a state of quasi-equilibrium had been reached[9] at the beginning of the series of distributions, i.e., the purely time-conditioned effect was negligible. The increasingly large development of free gas on collecting in the right-hand side of the system would appear to be due to the hysteresis effect associated with the sorption of easily condensible gases on glass surfaces. Exposure of the system to the low sulfur dioxide pressure obtaining at liquid air temperatures effects the release from the glass of quantities of gas, which are not resorbed immediately on raising the pressure again.

The effect may be considered to be the counterpart of the phenomenon observed by Burt and Jones.[10] These observers found that in a sorbing system where sorption was proceeding with extreme slowness it was possible to cheat time, as it were, by temporarily raising the working pressure. On returning the system to the original pressure the sorption was found to

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[8] It is not practicable to heat the taps of an apparatus during the outgassing and thus accelerate the liberation of dissolved gases from the lubricant, consequently the last traces are released with extreme slowness.

[9] The apparatus had been standing at low pressure for a fortnight before the series was commenced.

[10] F. P. Burt, loc. cit.

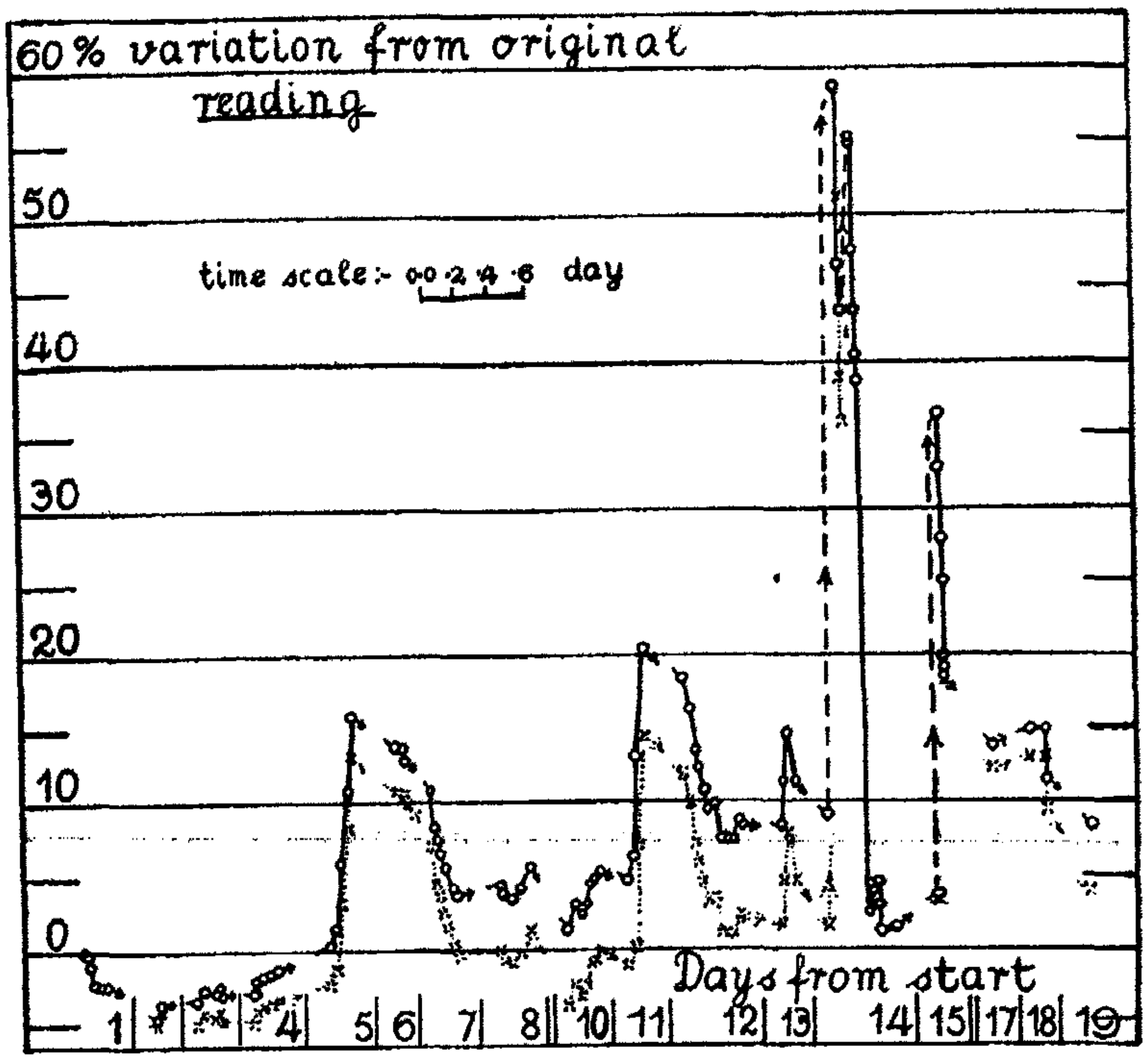

FIG. 3. VARIATION OF APPARENT FREE GAS IN SYSTEM PLOTTED AGAINST TIME FROM AN ARBITRARILY CHOSEN STARTING POINT

The lower, dotted line indicates that the truly time-conditioned desorption is practically nil; the main disengagement of gas is provoked by the low pressure resulting from the liquid air treatment.

The pressures obtaining at the distributions corresponding to the salient points of the curve were as follows:

	Left-hand side	*Right-hand side*
Start‡	0.00004 mm. Hg	0.08318 mm. Hg
1st peak‡ (5th day)	0.00030 mm. Hg	0.09640 mm. Hg
2nd peak‡ (11th day)	0.00278 mm. Hg	0.08626 mm. Hg
3rd peak* (13th day)	0.01519 mm. Hg	0.01497 mm. Hg
4th peak‡ (14th day)	0.00098 mm. Hg	0.1311 mm. Hg
5th peak‡† (14th day)	0.00049 mm. Hg	0.1289 mm. Hg
6th peak§ (15th day)	0.02306 mm. Hg	0.00010 mm. Hg

* After distributing throughout whole system.

† After removal of trace of permanent gas.

‡ Bulk of gas collected in right-hand side of system.

§ Bulk of gas collected in left-hand side of system.

have attained values which would not have been reached in reasonable time had the sorbing pressure been maintained constant throughout. In the present case we secure an increased desorption by temporarily reducing the pressure in the system to very low values.

The three peaks mentioned above (figure 3) are of interest for the light they throw on the loosely held surface gas in the system. Owing to the time required for the expanding gas to distribute itself throughout the different parts of the apparatus on evaporation some minutes elapse, after removal of the liquid air, before it is possible to take readings. Nevertheless, the three peaks are, qualitatively at least, in the relative positions we should expect to find in the case of a given quantity of sorbate admitted to (a) the whole, (b) the smaller part, and (c) the larger part, respectively, of a sorbing surface. Quantitative agreement is hardly to be expected in view of the difficulty of securing identical conditions in each case. If we suppose, however, that the relative positions of the peaks under consideration are, in the main, due to differences in the instantaneous sorption, it follows that the amount of gas actually condensed by the liquid air corresponds to a still greater departure from the initial reading than is indicated by the highest peak recorded in the figure, that of the fourteenth day.

CONCLUSIONS

From the foregoing it appears evident that, in an apparatus containing an easily sorbable gas at low pressures, there is, in addition to the free gas in the system as calculated from the known volumes and observed temperatures and pressures obtaining, an indeterminate amount of sorbed gas potentially available for release on reducing the pressure. This sorbed gas escapes observation under the usual conditions of experiment, though it may equal or even exceed in amount the free gas in the system. In the absence of time effects the gas would be difficult to detect, but by taking advantage of the time-lag in the attainment of sorption equilibria its presence may be revealed and an estimate, almost certainly too low, made of the amount involved.

In a typical apparatus containing sulfur dioxide a variation in the content of free gas amounting to more than 50 per cent referred to an arbitrary starting point, was observed. The ratio of surface to volume was not unduly large and the range of pressure variation in the system was from 0.0001 to 0.10 mm. of mercury, i.e., not excessively low.

Although the experiments described above were performed with sulfur dioxide in the system, the effect observed is in no way confined to this gas. It depends, as seen from figure 1, only on the relative shapes of the isochor and the sorption isotherm for the particular gas and apparatus concerned. Accordingly it may be expected to be present in any apparatus containing an easily sorbable gas at a sufficiently low pressure. Hence, in the absence of any control in the form of an independent method[11] of determining the quantities of substance involved, caution should be exercised in the interpretation of experimental results obtained under conditions similar to those considered above.

SUMMARY

1. Comparison of the forms of a typical sorption isotherm and the isochor of an apparatus of two-liter capacity indicate that, over a certain low pressure range, the gas sorbed on the walls of a relatively simple apparatus may approach or even exceed in amount that contained in the free space of the system.

2. In the absence of some independent form of control this sorbed gas may entirely escape detection, but by taking advantage of the time-lag in the attainment of equilibrium in the case of glass as sorbent we may nevertheless observe a part of the pressure-sensitive sorbed gas.

3. As an example, some measurements with sulfur dioxide are quoted, in the course of which a temporary disengagement of sorbed gas amounting to more than 50 per cent of the free gas at an arbitrary starting point was observed. The total quantity of sorbed gas in the system must have been still greater, since the instantaneous resorption could not be measured.

4. Attention is called to the necessity for exercising caution in the interpretation of experimental results involving measurements of pressure changes in apparatus containing easily sorbable gas at low pressures, viz., pressures below 0.1 mm. of mercury.

The experimental work on which this communication is based was performed at Frankfurt-am-Main during the tenure of a Fellowship awarded by the Alexander von Humboldt Stiftung, Berlin, to the Trustees of which the writer tenders his thanks.

[11] Such an independent form of control might be furnished, in sorption work for instance, by the McBain sorption balance or some other suitable form of microbalance.

SOME OBSERVATIONS ON THE TRANSFORMATION OF CYCLOPENTADIENE INTO ITS DIMERIDE

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Cyclopentadiene is obtained in the first runnings of the crude benzene from coal tar, and readily polymerizes, at temperatures up to 100°C., yielding chiefly dimeride. Above this temperature polycyclopentadienes are also formed. The present experiments, which arose out of work in another connection, consisted essentially of an investigation of the rate of dimerization, utilizing for this purpose the accompanying fall in vapor pressure.

EXPERIMENTAL

The crude dimeride was distilled and the fraction collected which boiled at 172.5°C. This was then redistilled and kept in a stoppered bottle in the dark. Some of the pure dimeride was boiled with iron filings in a flask fitted with a fractionating column. Ice-cold water was run through the condenser and the distillate collected in a receiver surrounded with ice, the fraction being employed which passed over at 41°C. This monomeride changed over very rapidly into the dimeride and was therefore used immediately after it had been prepared.

The apparatus employed was extremely simple and is shown in figure 1. The container for the liquid, A, which was similar in design to that described by Chaplin (1), was attached to the apparatus by a waxed ground-glass joint B. A T-piece, C, made connection with the manometer, D, a long tube dipping into a mercury reservoir, which was open to the air, while the other arm of the T-piece connected through the tap E with a Kraus mercury condensation pump, backed by a Hyvac oil pump. Before each reading the zero was taken, and since the individual experiments only took a short time, there was no change in the zero over this period. This was checked by remeasuring after each pressure reading had been taken.

In order to avoid the adjustment of a thermostat to the rather troublesome temperature of 12°C., which had been fixed as suitable for the comparison of vapor pressures, which would fall, during the course of the experiment, from the high value given by the monomeride to the much lower figure of the dimeride, measurements were always made at a series of neighboring temperatures, the results being plotted in the form of log

$p:1/T$. The container was kept at room temperature between the readings, and that chosen (12°C.) represented the average room temperature during the year in which the experiments were made.

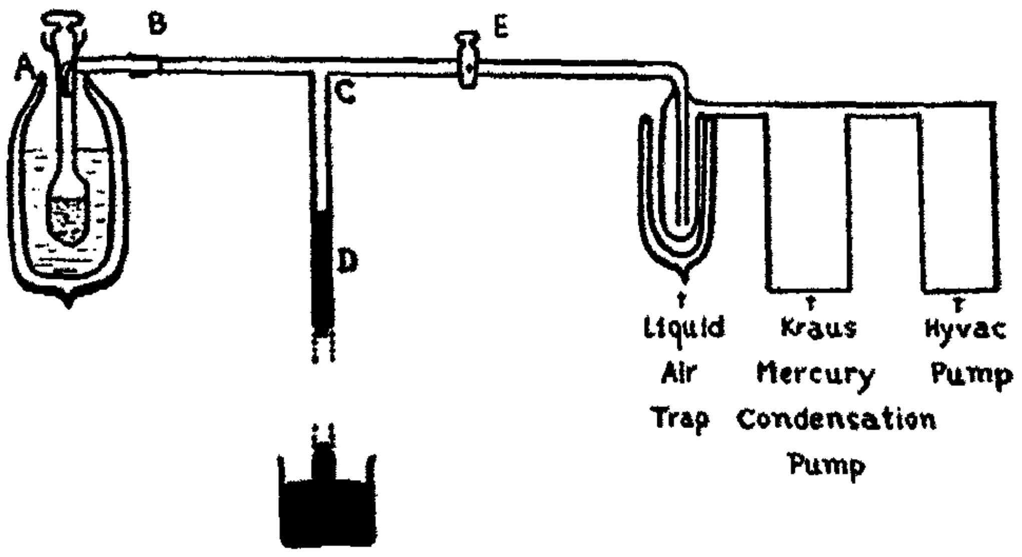

FIG. 1

TABLE 1

Zero reading = 27.98 cm.

TEMPERATURE	TIME AFTER OPENING CONTAINER	PRESSURE
degrees C.	*minutes*	*cm. Hg*
14.5	4	31.18
	7	31.22
	14	31.22
6.9	2	30.11
	6	30.25
	11	30.25
5.0	8	30.01
	17	30.01
0.0	12	29.51
	15	29.54
	46	29.54
−22.9	3	28.03
	8	28.18
	23	28.31
	34	28.40
	43	28.40

Two series of experiments have been carried out, in the first of which pure monomeride was introduced into the apparatus and the pressure read at various intervals over a period of approximately twelve months. In order to define the compositions giving rise to the above pressure a second series was carried out, in which definite mixtures were made and the pressures measured immediately. This gave a pressure–composition curve,

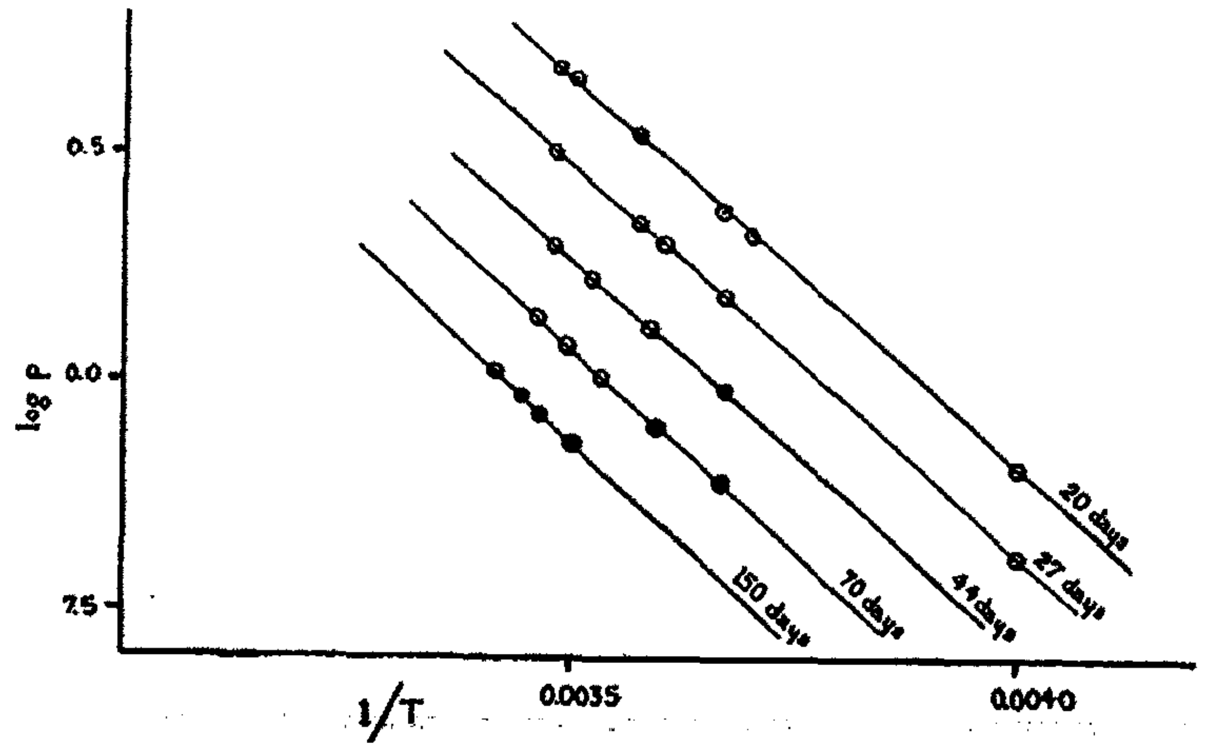

FIG. 2

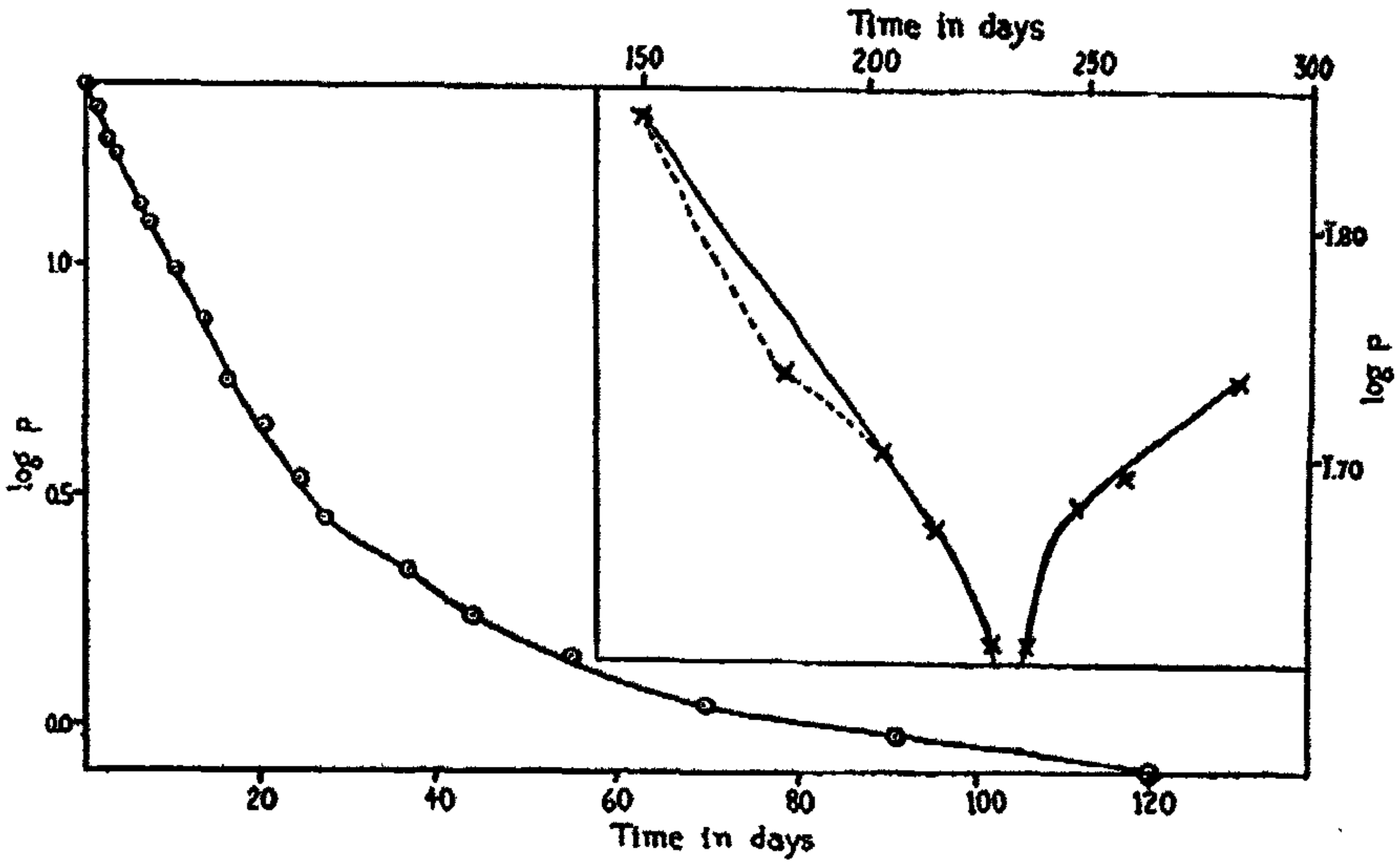

FIG. 3

and hence the pressure–time series could be converted into composition–time readings.

In table 1 the complete readings for the vapor pressure curve on the twenty-seventh day are given, and typical data expressed in figure 2, the pressures being in centimeters of mercury and the time in minutes.

The pressure figures at 12°C. were obtained from the log p: $1/T$ curves and are expressed in figure 3 which shows the change of pressure with time.

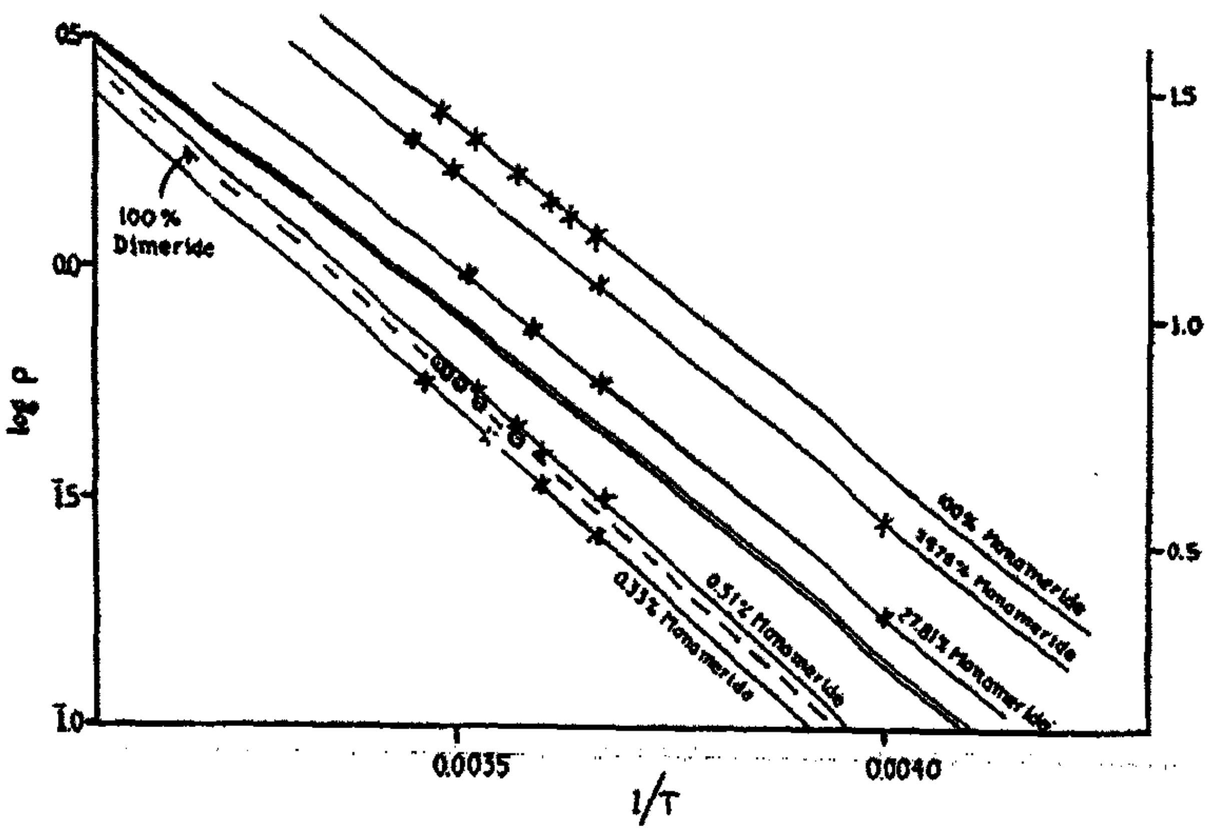

Fig. 4

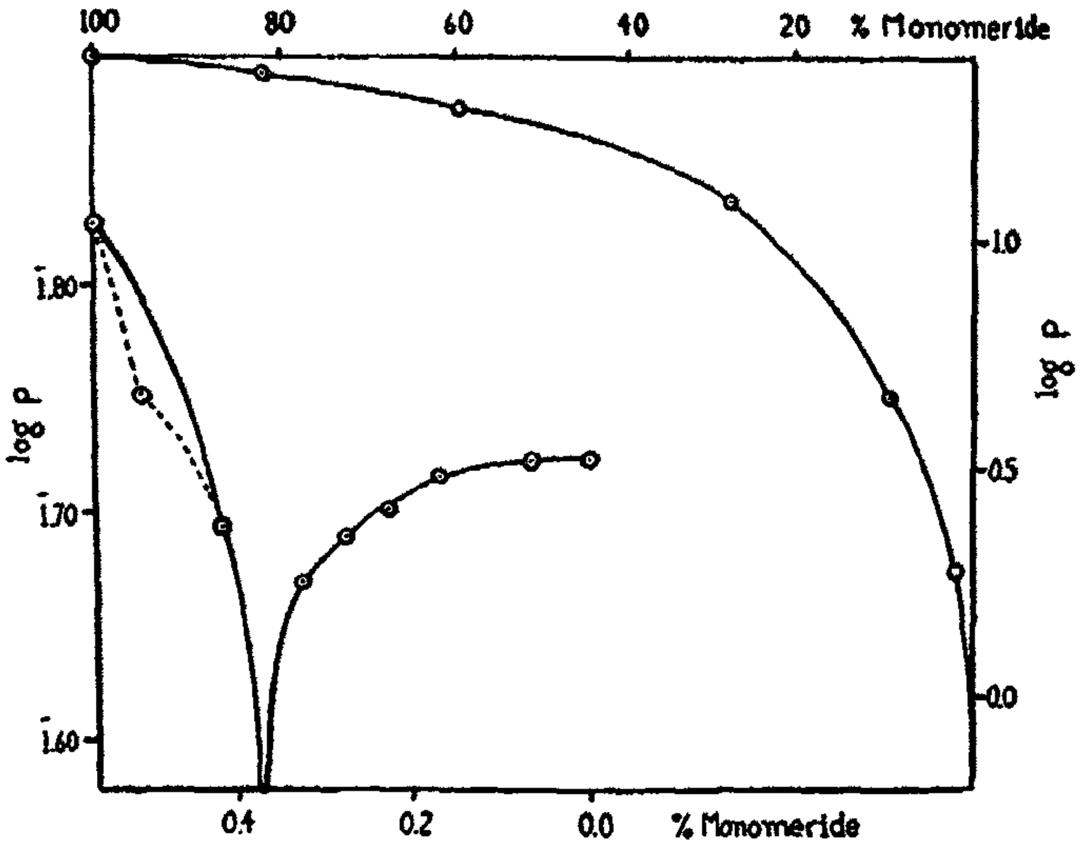

Fig. 5

A selection of curves from the second series is given in figure 4, the values at 12°C. being expressed in figure 5.

It will be seen that the vapor pressure curve passes through a minimum at a composition of approximately 0.36 per cent monomeride. This curve made it possible to calculate the composition at any point on the vapor pressure–time curve and hence the relation between per cent of monomeride and time has been obtained, the data being expressed in figure 6.

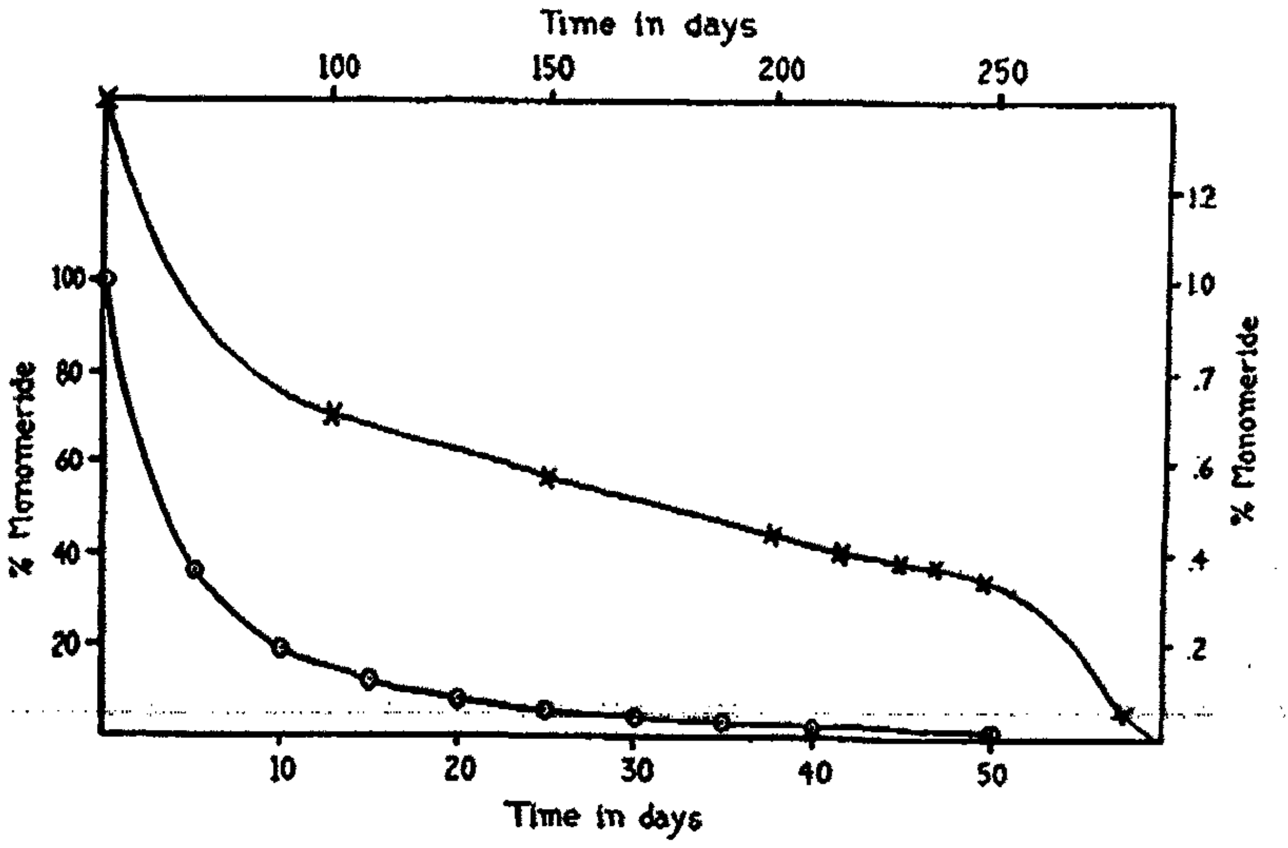

FIG. 6

DISCUSSION

One may regard the polymerization as proceeding for the one stage only (monomeride→dimeride) under the conditions of experiment, since the pressure finally remained constant over a considerable period. The chief point of interest, however, lies in the fact that the dimeride forms liquid crystals. It is now well established that liquid crystals are phases intermediate between the crystalline (solid) and amorphous (liquid) states. G. Friedel (2) considers that there may be two or possibly more such phases between the true crystalline and the true liquid forms. He then states that the order of succession must always be crystalline, smectic (soap-like), nematic (thread-like), liquid, and the reaction goes in this direction with increasing temperature or on dilution.

The present work showed that the dimeride exhibited these properties, for, after 150 days there was an appearance of thread-like bodies in the liquid, the latter becoming considerably more viscous, while after 181 days the solution set to a stiff opalescent jelly. On raising the temperature the reverse process took place. On the 203rd day the container was surrounded with ice for the lowest point, but the pressure obtained was abnormally high. On removing the ice bath it was found that practically the whole of the solution had changed to a crystal mass (dimeride), leaving only a small amount of liquor which was richer in monomeride than should have been the case if the liquid crystals had been present, thus causing the pressure to correspond to a composition of some weeks previously. After this point the 0°C. figure was omitted, the tendency for crystal formation being thereby largely removed. After 229 days the solution became more fluid as it approached the pure dimeride state.

When the solution was fluid equilibrium was rapid, but as soon as liquid crystals had formed it was very slow. The points in figure 2 which were in contact with the smectic mesophase have been marked with solid circles. A survey of the curves showed that the form was the same, whether the solution with which it was in contact was liquid or contained liquid crystals, at any rate to within experimental error over the range measured.

After one year the monomeride had completely changed into the dimeride and there was no evidence from the vapor pressure measurements that the change was proceeding further. At the close of the experiment the liquid had a slight opalescence, but there was no trace of resin formation. However, on exposure to air the liquid turned yellowish in color with distinct rapidity. From this it would appear that only the reaction, monomeride → dimeride, takes place in a vacuum, but that it proceeds to a resin in the presence of air.

It would appear quite probable that the dotted lines in figures 3 and 5 represent the correct curves, since the pressure is about the same amount below the smooth curve in each case, and as one is obtained from the monomeride→dimeride series and the other is the vapor pressure of a definite mixture, this cannot be a chance agreement. On the basis of the phase rule, the two forms of liquid crystal are considered to be distinct phases and will therefore give rise to invariant points on the phase diagram. There are not enough points to show the position of each section of the curve, but the presence of a point so far removed from the smooth curve shows that the latter is discontinuous.

The mesophases would appear to exert a considerable influence on the reaction-time curve. For example, reference to figure 6 shows that the amount of monomeride steadily decreases up to a period of 93 days, at which point approximately 0.73 per cent remains. From this point up to a period of 235 days the curve is almost linear, and represents an extremely slow rate. From 235 days onwards, however, the change is again much more rapid. Between the two periods mentioned the liquid phase contained liquid crystals, and hence, the reason for the slow rate of change over this period may be due to hindrance to diffusion of the molecules in the solution, owing to the resistance occasioned by the presence of these liquid crystals.

SUMMARY

1. The vapor pressure of a cyclopentadiene has been measured at various temperatures during the change from 100 per cent monomeride to 100 per cent dimeride.

2. The vapor pressures of known mixtures of monomeride and dimeride have been determined at various temperatures.

3. The formation of liquid crystals has been observed and the conditions noted.

The authors with to express their thanks to Professor A. J. Allmand for the interest that he has taken in this work.

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THE RATE OF BROMATE FORMATION IN AQUEOUS SOLUTIONS CONTAINING HYPOBROMOUS ACID AND ITS ANION

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In connection with other kinetic investigations, we have found it convenient to prepare aqueous solutions containing hypobromous acid by adding bromine to a phosphate buffer solution containing silver ion;[1] as hydrogen ion and bromide ion are rapidly removed, the hydrolysis equilibrium of bromine is shifted,

$$Br_2 + H_2O \rightleftharpoons HBrO + H^+ + Br^- \qquad (1)$$

and the concentration of hypobromous acid is increased. Although the rate laws given by Skrabal and Weberitsch (1) for the reaction[2]

$$5HBrO = BrO_3^- + H^+ + 2Br_2 + 2H_2O \qquad (2)$$

indicate that[3] (HBrO) in our solutions should decrease to half its value in, say, 10^{-2} seconds, we found that approximately twenty-four hours elapsed before so much decomposition occurred. Duplication of part of the work of Skrabal and Weberitsch has convinced us that their results are entirely reliable, and that the source of this surprising conflict must consequently

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[1] After several unsuccessful attempts to prepare aqueous solutions containing only hypobromous acid by the distillation methods recommended in the older literature led us to conclude that this could not be accomplished, we discovered that Pollak and Doktor (Z. anorg. allgem. Chem. 196, 89 (1931)) had already reached this conclusion as a result of similar experiments.

[2] The stoichiometric equation for the formation of bromate ion will assume different forms under different experimental conditions. BrO^-, Br_3^-, or Br_2 may appear as reactant instead of HBrO, and what substances, in addition to BrO_3^-, appear as resultants is also subject to change. Decomposition of bromine compounds to yield oxygen is negligible under all experimental conditions with which we have here to deal.

[3] As in other communications, the following conventions will be observed: ( ) means "concentration of" in moles per liter; the units for all specific rates are moles, liters, minutes; when no temperature is specified, 25°C. (or nearly 25°C.) is meant; $\rightarrow$ will be restricted to steps which may be rate-determining. Rate laws will usually be referred to by letter only; the proper letter used as subscript will indicate to which law a specific rate constant belongs.

be sought in their interpretation of these data. We have concluded that much of the conflict has resulted from several errors, which we shall point out, and that our preliminary rate measurements, some twenty in number, indicate how the mechanism of reaction 2 may be directly investigated. We have no intention at present of undertaking a further investigation ourselves.

In table 1 are summarized the rate laws that should govern the stability of hypobromous acid in all solutions not strongly alkaline. We shall now consider evidence to show that C (or C′) is more plausible than B (or B′), that A is not experimentally established, and that the kinetic data upon which table 1 is based can be interpreted in terms of the rate-determining step

$$2HBrO + BrO^- \rightarrow BrO_3^- + 2H^+ + 2Br^- \qquad (3)$$

given by Kretzschmar (2). (The intimate mechanism of this rate-determining step will be discussed later.)

To secure data that may aid in deciding the relative plausibility of B′ and C′ (or, of B and C) we have measured the stability of hypobromous acid in phosphate buffer solutions at the low (Br^-) insured by the presence of Ag^+. These experiments, given in table 2, together with all others in which the rate of disappearance of hypobromous acid was measured, were carried out as follows. The reaction mixture, contained in a glass-stoppered flask and shielded from direct sunlight, was placed in a thermostat at 25°C. At convenient intervals samples were withdrawn, run into an iodide solution containing $H_2PO_4^-$, and titrated with 0.004 N thiosulfate. Calculations and blank tests concurred in showing that the bromate present was not reduced rapidly enough under the conditions employed to cause any error in the titration.

The experimental results in table 2 agree in order of magnitude with the rates calculated from C′—but not at all with those from B′. Further, the actual rate at which hypobromous acid disappears under the above conditions is (virtually) *independent* of (Br^-), in agreement with C′ but not with B′. Our experimental evidence, joined to that of Skrabal and Weberitsch (X, Versuche 11 to 14 inclusive), has convinced us that of the two rate laws C′ is far the more plausible. We must admit, however, that the proof is not complete; for, as will appear later, extension of the results in table 2 has not permitted the deduction of a definite rate law.

Skrabal and Weberitsch were led to adopt B because this differential equation, when properly combined with that for the reduction of bromate by bromide ion in acid solution, gave the equilibrium constant for reaction 2 (X, pp. 249–52); we are not certain that this agreement between a quotient of specific rates and an equilibrium constant warranted changing

TABLE 1

Summary of rate laws for reaction 2

These laws are intended to govern $-d\Sigma(Br_2)/dt$ except in strongly alkaline solutions; $\Sigma(Br_2) = (Br_2) + (Br_3^-) + (HBrO)$

RATE LAW	SPECIFIC RATE AT 25°C.	CONCENTRATION TERMS	REFERENCE	COMMENT
A	$6.5(10^4)$	$\frac{(OH^-)(Br_3^-)^2}{(Br^-)^2}$	X,* p. 244 et seq.	Adopted for their "rapid reaction" by S. and W.
B	$8.3(10^{22})$†	$\frac{(OH^-)^4\,(Br_3^-)^3}{(Br^-)^7}$	X, p. 246 et seq.	Adopted for their "slow reaction" by S. and W.
B′	$2.7(10^9)$†‡	$\frac{(HBrO)^3\,(OH^-)}{(Br^-)}$		Alternative form‡ of B
C	$2.4(10^{23})$†	$\frac{(OH^-)^4\,(Br_3^-)^3}{(Br^-)^6}$	As for B	Given directly by the experimental evidence. Not adopted by S. and W. because they considered B more plausible.
C′	$7.9(10^9)$†‡	$(HBrO)^3\,(OH^-)$		Alternative form‡ of C
C″	Definite value cannot be given	$(HBrO)^3\,(BrO^-)$	Kretzschmar (2)	Alternative form§ of C

* See reference 1.

† We have calculated these specific rates from Versuch 14 (X, p. 248), employing for this purpose the correct concentrations: namely, $(Br_3^-) = 0.059$ and $(Br^-) = 0.34$. In their calculations, Skrabal and Weberitsch assumed (mistakenly) $(Br_3^-) = \Sigma(Br_2) = 0.07$, and obtained $k_B = 3.8(10^{22})$; the difference between this and $8.3(10^{22})$, which corresponds to the correct concentrations, serves to emphasize how sensitive are specific rates involving high orders to relatively small concentration changes.

Versuche 11, 12, and 13, for which Skrabal and Weberitsch did not evaluate k_B, give for $k_C(10^{-23})$, respectively, 1.9, 3.9, and 2.3; these, together with the value $2.4(10^{23})$, given above, show what concordance may be reasonably expected from such measurements.

‡ B and B′ are alternative forms of one rate law, C and C′ of another, for the equilibrium

$$HBrO + 2Br^- \rightleftharpoons Br_3^- + OH^- \qquad (4)$$

is always maintained; the value of its equilibrium constant, the cube of which is involved in each transformation, is (X, p. 245; see reference 1)

$$\frac{(Br_3^-)\,(OH^-)}{(HBrO)\,(Br^-)^2} = 3.2(10^{-5}) \text{ at } 25°\text{C}.$$

§ The identity of C′ and C″ is made obvious by writing

$$(BrO^-) = 1/K_{hyd.}(HBrO)\,(OH^-)$$

the uncertainty in the value of $K_{hyd.}$ precludes giving an exact value for $K_{C''}$.

the experimentally derived halide term[4] in C to that in B. We wish to emphasize that the specific rate of reaction 3 need stand in no simple relation to the equilibrium constant of reaction 2.

The experimental evidence in X (see reference 1) upon which A is based involves Versuche 5, 6, and 7 (Versuche 8, 9, and 10 deal with the influence of electrolytes); of these, Versuch 6 is used in the calculation of the specific rate. In this calculation (X, p. 244) there is implicit the assumption that the rate due to C′ (or to B′) is *negligible*. At $t = 15$, $-d\Sigma(Br_2)dt$ in Versuch 6 was $1.4(10^{-4})$ moles per minute per liter; from C′ we calculate a corresponding rate, in these units, of $114(10^{-4})$; and from B′, of $39(10^{-4})$; these calculations may be verified by use of the data in table 3. The magnitudes of these rates leave no doubt that C′, which we have adopted as more plausible than B′, must be considered in the interpretation of these data; indeed, they suggest that all the observed rate in Versuch 6 may be due to reaction 3, for which C′ is one form of the rate law.

TABLE 2

Rate of disappearance of hypobromous acid in potassium phosphate buffer solutions at $(HBrO) = 5(10^{-4})$

EXPERIMENT	$(OH^-)10^{5}$*	$(Br^-)10^{9}$†	RATES IN MOLES PER LITER PER MINUTE × 10^{8}		
			B′	C′	Measured
8	0.67	1	2.2 × 10^{8}	0.66	2.2
19	1.15	1.2	3.3 × 10^{8}	1.1	19
15	4.8	2.6	6.2 × 10^{8}	4.7	46
17	19.6	5.2	12.7 × 10^{8}	19	71
6	47	4.3	37 × 10^{8}	46	21
7	47	13 × 10^{6}	12 × 10^{3}	46	13
5	52	7 × 10^{5}	2.5 × 10^{4}	51	17

* (OH^-) was calculated from the data given by Cohn (J. Am. Chem. Soc. **49**, 173 (1927)); we need not distinguish between (OH^-) and its activity. In experiments 5, 6, 7, and 8, total phosphate was 0.05 *M*; in the others, 0.2 *M*.

† Values of (Br^-) are approximate; except in experiments 5 and 7, silver bromide and (usually) silver phosphate were present as solids; in these cases, (Br^-) was calculated from $(Ag^+)(Br^-) = 5.3(10^{-13})$ and (when necessary) from $(Ag^+)^3(PO_4^{---}) = 1.6(10^{-18})$.

And this suggestion becomes more plausible when we observe the constancy of k_3 in Versuch 6, a constancy also found in Versuche 5 and 7. (We do not believe that k_2 is, in any of these experiments, sufficiently constant to permit the valid derivation of a rate law.) Even if we adopt k_3, and thus the $(Br_3^-)^3$ term, we have yet to show that the rate obeys not the (OH^-) and $1/(Br^-)^3$ terms in A, but the $(OH^-)^4$ and $1/(Br^-)^6$ terms in C. We observe next that the orders given in A for these concentrations were

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[4] We have duplicated Versuche 11 and 14 (X, p. 247) and found $1/(Br^-)^{6.1}$ for the halide term; Skrabal and Weberitsch obtained $1/(Br^-)^{5.8}$.

not correctly calculated, and for this reason: They were obtained from the effects on k_2 of changing (OH^-)—Versuche 5 and 6— and Br^-—Versuche 5 and 7. But k_2 involves

$$\Sigma(Br_2) = (HBrO) + (Br_2) + (Br_3^-)$$

Manifestly, altering either (OH^-) or (Br^-) will alter the distribution of $\Sigma(Br_2)$ among these three terms (cf. reaction 4); if at least two of these are of appreciable magnitude, this change in distribution will be reflected in the rate; in comparing values of k_2 from two experiments designed to determine the order with respect to some reagent, this change must be considered, or an erroneous result will be obtained. We have allowed for this change in calculating the orders given in table 4, in which a comparison of the seventh and eighth columns will reveal the importance of considering the distribution of $\Sigma(Br_2)$. (See also the last four columns in table 3.)

TABLE 3

*Recalculation of Versuch 6**

$(OH^-) = 2.1(10^{-5})\ M$; $(Br^-) = 1.0\ M$

t	$(Br_2)10^3$	$(Br_3^-)10^3$	$(HBrO)10^3$	k_2†		k_3†	
				S. and W.	Corrected	S. and W.	Corrected
0	0.50	8.15	5.30				
15	0.39	6.32	4.11	1.36	3.93	112	549
30	0.33	5.35	3.47	1.10	3.18	112	549
75	0.24	3.90	2.49	0.90	2.60	116	568

* X, p. 241. cf. also X, p. 244.

† The units for all specific rates are moles, minutes, liters. (To express the specific rates in X in these units, the k_2 given there must be multiplied by $2(10^3)$, and the k_3 by $4(10^6)$).

The "S. and W." rate constants are defined by

$$-\frac{d\Sigma(Br_2)}{dt} = k_2\Sigma(Br_2)^2 = k_3\Sigma(Br_2)^3$$

The "corrected" rate constants are defined by

$$-\frac{d\Sigma(Br_2)}{dt} = k_2(Br_3^-)^2 = k_3(Br_3^-)^3$$

at constant (OH^-) and (Br^-).

The terms $(OH^-)^{3.7}$ and $1/(Br^-)^{5.9}$ are in satisfactory agreement with those to be expected from C. Taken by themselves, the results in table 4 are as good evidence for C as can be adduced from any other experimental work in X; for the k_C values in table 4 agree as well among themselves as do those from the phosphate buffer solutions (cf. table 1, footnote†). The average of the latter, $2.4\ (10^{23})$, is some seventyfold greater than 3.5

(10^{21}), the mean of the values in table 4; we hesitate to ascribe all this difference to equilibrium salt effects, although these will be unusually large in the reaction system with which we are dealing. (If the rate-determining step, reaction 3, is correct, the $1/(Br^-)^6$ term, to give one example, will be due entirely to equilibria preceding this step; such a state of affairs makes for large salt effects.) Nevertheless, we have concluded that there is evidence in X for only one rate law, C, for which the rate-determining step is reaction 3; the numerical value of the corresponding specific rate is uncertain.

TABLE 4

*Carbonate-bicarbonate buffer solution experiments used to establish rate law A**

VERSUCH	Br^-	$(Br_2)10^3$	$(Br_3^-)10^3$	$(HBrO)10^3$	$(OH^-)10^4$	k_3†		$k_C(10^{-21})$	$k_C'(10^{-9})$
						S. and W.	Corrected		
5	1.0	0.58	9.41	3.01	1.04	16	42.3	3.8	1.24
6	1.0	0.33	5.35	3.47	2.08	113	552	3.0	0.97
7	0.51	0.31	2.53	3.16	1.04	188	2520	3.8	1.24

Variation of k_3 with (OH^-): From Nos. 5 and 6: $\frac{552}{42.3} = \left[\frac{2.08}{1.04}\right]^x$; $x = 3.7$. Rate $\propto (OH)^{3.7}$

Variation of k_3 with (Br^-): From Nos. 5 and 7: $\frac{2520}{42.3} = \left[\frac{1.0}{0.51}\right]^y$; $y = 5.9$. Rate $\propto \frac{1}{(Br^-)^{5.9}}$

* X, p. 241.

† Cf. footnote†, table 3. In our definition of $\Sigma(Br_2)$, (BrO^-) has been omitted. In justification of this procedure we mention that it is simplest, and that (BrO^-) cannot be calculated until the dissociation constant of HBrO is known. We observe that considering (BrO^-) tends to increase both k_C and the orders obtained for (OH^-) and $1/(Br^-)$: thus, assuming $K = \frac{(H^+)(BrO^-)}{HBrO} = 10^{-9}$, gives $(OH^-)^{5.3}$ and $1/(Br^-)^{7.1}$, while assuming $K = 10^{-10}$ scarcely changes the results in table 4. Since the assumption of the larger value leads to no simple kinetic conclusions, we have preferred omitting (BrO^-) from consideration, a procedure tantamount to assuming for K a value of 10^{-10}, or less. If our kinetic interpretation of the data in table 4 is correct, further experiments of the same sort over a range of OH^- concentrations may provide a way of obtaining the dissociation constant of HBrO from kinetic data.

Kretzschmar (2) in 1904 completed the first extensive kinetic investigation of reaction 2. He presents kinetic evidence (reference 2, pp. 794–8) for reaction 3 as a rate-determining step; this interpretation he considers plausible because reaction 3 is analogous to the rate-determining step found by Foerster and Jorre (3) for the formation of chlorate ion through the decomposition of hypochlorous acid. Kretzschmar made rate measurements on solutions of hypobromous acid, prepared by distillation, to which had been added a known amount of potassium hydroxide; he assumed that one mole of added base yielded one mole of hypobromite ion. His measurements give for C a specific rate of approximately $3(10^{19})$,[5] which is to be compared with the values $2.4(10^{23})$ (phosphate buffer) and $3.5(10^{21})$ (carbonate–bicarbonate buffer) obtained from the measurements of Skrabal and Weberitsch. In explaining why Kretzschmar obtained such low values for k_C, two things, in addition to salt effects, must be considered: first, our experience indicates that his hypobromous acid solutions probably contained (H^+) at an appreciable, though unknown, concentration; and second, when base is added to an hypobromous acid solution the amount of BrO^- formed depends upon the dissociation constant of this acid, which is not definitely known.

Our review of the rate laws in table 1 is now complete and leads to this conclusion: Over a wide range of experimental conditions, the law that governs the rate of reaction 2 is formally identical with C″, as found by Kretzschmar (2), and assumes more complex forms (e.g., C) as the composition of the reaction mixture changes. We observe that one form (C″) of this law is analogous to that found by Foerster and Jorre (3) for hypochlorous acid solutions, while another (C) corresponds to one found by Skrabal (4) for the formation of iodate ion. It appears, therefore, that the law

$$-d\Sigma(X_2)/dt = k(HXO)^2(XO^-) \qquad (5)$$

is of general importance in the formation of the halate ion, XO_3^-, through the decomposition of these lower-valent halogen compounds. This law obviously suggests

$$2HXO + XO^- \rightarrow XO_3^- + 2X^- + 2H^+ \qquad (6)$$

as a rate-determining step; when we come to consider, however, what the intimate mechanism of reaction 6 might be, we are faced with several possibilities, of which none can be definitely eliminated. That reaction 6 is trimolecular—i.e., that it involves only triple collisions—seems very improbable; and this justifies the assumption that an equilibrium is involved. The compound $X_3O_2^-$, which has been postulated by Skrabal (4) and favored by Bray (5), may be assumed; but the mechanism

$$\text{Equilibrium: } 2HXO + XO^- \rightleftharpoons X_3O_2^- + H_2O \text{ (or } H_2X_3O_3^-) \qquad (6a)$$
$$\text{Rate-determining: } X_3O_2^- + H_2O \rightarrow XO_3^- + 2X^- + 2H^+ \qquad (6b)$$

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[5] Kretzschmar's data give $k_{C''} = 100$ at 25°C. (cf. reference 2, p. 798); to convert them to our units, his specific rates must be multiplied by 400. If 10^{-10} is assumed to be the dissociation constant of hypobromous acid (this corresponds to a hydrolysis constant for BrO^- of 10^{-4}), then $k_{C'} = 100/10^{-4}$, or 10^6; and $k_C = 10^6/[3.2(10^{-5})]^3$, or $3(10^{19})$.

does not exhaust the possibilities. No matter what mechanism is chosen, however, the simplest procedure, and therefore most logical so long as no conflict with experiment is involved, will be to consider it valid for all the halogens.

Kretzschmar (reference 2, pp. 790–3) also measured the rate of decomposition of hypobromite solutions, which proved to be surprisingly stable. He attempted no kinetic evaluation of these results, but he considered the mechanism

$$3BrO^- \rightarrow BrO_3^- + 2Br^- \qquad (7)$$

not improbable. In most of his experiments the concentration changes are not appreciable enough to permit the certain deduction of a mechanism; for Uebersicht 3, however, we have found that the rate law is[6]

$$-\frac{d(BrO^-)}{dt} = 0.056\ (BrO^-)^2 \text{ at } 80°C. \qquad (8)$$

corresponding to the rate-determining step

$$2BrO^- \rightarrow BrO_2^- + Br^- \qquad (9)$$

Assuming that this rate law is valid also in the experiments at lower temperatures, we have calculated that the rate of reaction 9 at any temperature is given by

$$-\frac{d(BrO^-)}{dt} = 10^{14}\, e^{-\frac{2.5(10^4)}{RT}}\ (BrO^-)^2 \qquad (10)$$

Within the experimental error, which is rather large,[7] the Arrhenius constant of reaction 9 is identical with the collision number. (10^{13} moles per liter per minute is the collision number for a bimolecular gas reaction at unit concentration of the reactants.) The stability of these hypobromite solutions might be utilized in the preparation of hypobromous acid.

Equation 8 is formally identical with the rate law found by Foerster and Dolch (6) to govern the stability of hypochlorite solutions, and this circumstance is additional evidence for our interpretation of Kretzschmar's

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[6] The specific rate was calculated for $(OH^-) = 1.89$; in such basic solutions, (HBrO) is probably negligible, for the rate is (virtually) independent of (OH^-). Since the change in (Br^-) that took place during the experiment was not reflected in the rate, we conclude that (Br^-) does not belong in the rate law.

[7] We estimate the error in the heats of activation in equations 10 and 12 to be ±2000 calories; there is, of course, a corresponding uncertainty in the values of the Arrhenius constants.

results. From the data given by Foerster and Dolch for 25, 50, and 90°C., we have calculated that the rate of the reaction[8]

$$2ClO^- \rightarrow ClO_2^- + Cl^- \qquad (11)$$

at any temperature is given by

$$-d(ClO^-)/dt = 10^{12}\, e^{-\frac{2.5(10^4)}{RT}}\, (ClO^-)^2 \qquad (12)$$

Although the experimental error is rather large, there is no doubt that the analogous reactions 9 and 11 have almost identical Arrhenius constants and heats of activation.

We shall close with a brief discussion of our rate measurements. Although the rate was followed until nearly all the HBrO had disappeared in some twenty reaction mixtures like those of table 2, no definite order could be established either for (HBrO) or for (OH^-); the one most nearly obeyed with respect to (HBrO) is the second; with respect to (OH^-), the order is not higher than the first. Under some conditions the second order constant with respect to (HBrO) decreased as the run progressed, often it increased, and sometimes it remained unchanged. In all probability we are dealing here with a mixture of reactions, and a change of temperature or of (OH^-) might do much to simplify matters. At any rate, the fact that the rates we measured are independent of (Br^-) leaves little doubt that the rate at which HBrO decomposes into bromate is being measured directly, i.e., that no equilibria are maintained in front of the rate-determining steps. In addition to reaction 3, a second step of the type

$$HBrO + HBrO_2 \rightarrow BrO_3^- + 2H^+ + Br^- \qquad (13)$$

may be involved.

SUMMARY

1. In agreement with the results of Pollak and Doktor (7), it has been found impossible to prepare, by distillation, aqueous solutions containing only hypobromous acid.

2. At low (Br^-), solutions of HBrO are far more stable than one law given by Skrabal and Weberitsch (1) for the rate of the reaction

$$5HBrO = BrO_3^- + 2Br_2 + H^+ + 2H_2O \qquad (2)$$

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[8] At low (OH^-) the rates measured by Foerster and Dolch were independent of (OH^-) and, within limits, of (Cl^-), which nearly doubled in magnitude as some of their experiments progressed (cf. Uebersicht 1, reference 6, p. 140). We see no reason for doubting the plausibility of the above mechanism (in this connection cf. reference 6, p. 144).

allows; a reëxamination of their kinetic evidence has led to the conclusion that, except in strongly alkaline solution, the rate of reaction 2 should be governed by

$$-d\Sigma(\mathrm{Br_2})/dt = k_{C''}(\mathrm{HBrO})^2\,(\mathrm{BrO^-})$$

(At 25°C., widely different values, ranging from approximately 10^2 to nearly 10^6, have been obtained for $k_{C''}$ under different experimental conditions.) In this, its simplest form, the rate law is identical with that found by Kretzschmar (2); further, it appears not irreconcilable with the stability we have observed in our hypobromous acid solutions.

3. Since this rate law is analogous to those found for the formation of ClO_3^- and IO_3^- under certain experimental conditions, it has been concluded that the rate-determining step

$$2\mathrm{HXO} + \mathrm{XO^-} \rightarrow \mathrm{XO_3^-} + 2\mathrm{X^-} + 2\mathrm{H^+} \qquad (6)$$

is of general importance in the formation of halate ions through the decomposition of the halogens (or substances in equilibrium with them).

4. The intimate mechanism of the rate-determining step, reaction 6, cannot be definitely settled; an intermediate compound, like $X_3O_2^-$, in equilibrium with HXO and XO^- (and, consequently, with X_3^-, X_2, and X^-) may be involved, for reaction 6 is probably not the result of triple collisions alone.

5. From the measurements of Kretzschmar (2) in strongly alkaline solution, we have deduced the rate law

$$-d(\mathrm{BrO^-})/dt = 0.056(\mathrm{BrO^-})^2 \text{ at } 80°\mathrm{C}. \qquad (8)$$

corresponding to the rate-determining step

$$2\mathrm{BrO^-} \rightarrow \mathrm{BrO_2^-} + \mathrm{Br^-} \qquad (9)$$

which is analogous to that found by Foerster and Dolch (6) in ClO^- solutions. Reaction 9 and its ClO^- analogue have nearly identical heats of activation and Arrhenius constants.

6. Our rate measurements, as well as those of Pollak and Doktor (7), on reaction 2, indicate a need for further work, which we have no intention at present of undertaking.

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III. THE EFFECT OF THE ALKALI AND THE ALKALINE EARTH IONS ON THE ADSORPTION OF THORIUM B BY SILVER BROMIDE CRYSTALS

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INTRODUCTION

In previous studies of the relative adsorption of a series of similar ions on polar crystal surfaces, attention has been given to the variable surface of the crystals and to the effects of the addition of foreign ions. In the early work the precipitates were formed in the presence of the material to be adsorbed, thereby introducing such errors as (1) variable surfaces of the precipitates, (2) occlusion of the adsorbed material, and (3) effects due to the presence of the ions formed as by-products in the precipitation reaction.

Fajans (1) in his recent work used carefully dried powders and added radioactive ions as nitrates and the other anions and cations as nitrate and potassium salts. The value of such studies in the field of adsorption is in the possibility of formulating a theory based on quantitative data from observations made on the simplest possible system. Even with the simple systems used by Fajans and others, complications arise. For instance, in the study of the adsorption of thorium B, the simplest possible system may consist of silver iodide crystals in contact with a solution containing as many ions as ThB^{++}, Ag^+, I^-, H^+, OH^-, NO_3^-, Br^-, K^+, and ions from the glass vessels. Then there is the possibility of the adsorption of the thorium B on the walls of the glass vessels and the complications introduced by the formation of other substances by the interaction of the ions listed.

Silver bromide crystals in contact with a solution of potassium bromide acquire a negative charge due to the adsorption of bromide ions. This charge can be shown by a simple cataphoresis experiment or by measuring the amount of the positively charged ThB^{++} ions which can be adsorbed from the solution. Increasing the concentration of the potassium bromide in the solution increases the charge on the crystals and increases the amount of the thorium B adsorbed. Qualitatively, we can say that the additional bromide ions on the surface of the silver bromide crystals mean an increased adsorption of thorium B, but in measurements of the per cent adsorption versus concentration of potassium bromide in solution, we are dealing not only with changing concentrations of ThB^{++} ions and Br^- ions but also with changing concentrations of potassium ions. It is true that, according to the adsorption rule that an ion will be adsorbed if it forms an insoluble compound with the oppositely charged ions of the crystal, very little adsorption of potassium ions would be expected. However, it has been shown (2) that a large concentration of an ion forming a soluble compound with the oppositely charged ion of the crystal will repress from the surface of a crystal adsorbed ions which form very much less soluble compounds. In other words, all ions possess some tendency to be adsorbed or attracted to the surface of a polar crystal. It is only, then, by studying behaviors of different ions alone and in the presence of each other that an accurate adsorption rule can be formulated.

In this work we are interested in the amount of adsorption of thorium B by silver bromide crystals in the presence of varying concentrations of bromide ions and in the part played by the cation of the bromide salt used. Fajans and Erdey-Grúz (3) observed that whereas potassium bromide decreased the amount of erythrosin adsorbed on silver iodide, potassium chloride increased it. King and Pine observed that whereas potassium bromide increased the amount of thorium B adsorbed on thallium iodide, potassium chloride decreased it. The explanation can be given in both cases that this is due to the potassium ions. If potassium ions are changing the charge on the adsorbent, or replacing the adsorbed material from the surface of the adsorbent or being adsorbed along with the material whose concentration is being measured, then there should be certain properties of the potassium ion which determine the part it plays and whose effect can be measured. In this event, if the bromide ion concentration is kept constant and the potassium ion concentration is varied, or if the potassium ion is replaced by another cation, some information about these properties should be obtained. In this paper will be reported the data which was gathered from the measurements made on the adsorption of thorium B on silver bromide from solutions of varying concentrations of the different alkali and the alkaline earth ions.

PREPARATION OF MATERIALS

The water used was made in the same way as that used in the work by King and Pine (1).

Silver bromide

The silver bromide powder used for all the work was prepared according to the method of J. Walker (4). "Tested Purity" silver bromide was dissolved in C.P. ammonium hydroxide (specific gravity 0.9) and then reprecipitated by diluting the ammonia solution with water. Ten liters of the ammonium hydroxide were placed in a 12-liter balloon flask and saturated with the silver bromide by stirring and warming. The solution was then allowed to stand at room temperature, and 100 cc. of the clear solution was run into 400 cc. of water with constant mechanical stirring. The precipitate was allowed to settle and collected by decanting the supernatant liquid. A large amount of precipitate was collected and placed in the washing tower as described in the work of King and Pine. This was washed with stirring continuously, the water being made by distillation in the Barnstead still and run through Pyrex tubing through the wall of the dark room. It was dried in an electric oven at 115°C. and then stored over phosphorus pentoxide in a desiccator. All work with the silver bromide was done in the dark room, using Eastman safelights for illumination.

Bromide salts

The solutions of C.P. or T.P. salts were standardized gravimetrically by precipitating silver bromide or volumetrically against standard silver nitrate, using potassium chromate as an indicator.

The rubidium bromide was Eimer and Amend's "Tested Purity" grade and the cesium bromide was specially prepared here in the laboratory by Professor Mears.

The radioactive solutions were prepared as described in the work of King and Pine and the method of measurement was the same as that used in the work of King and Romer (5).

METHOD OF PROCEDURE

The glassware had the same attention as that used in the work by King and Pine. The pure silver bromide powder was weighed into brown bottles in the dark room. Samples weighing 0.5000 ± 0.0002 g. were used. The correct amounts of acid (see section 6), bromide salts, and nitric acid solution of thorium B were added and the mixture was shaken for 45 minutes. After the settling of the precipitate or after centrifuging, a 5-cc. sample of the supernatant solution was taken for evaporation and activity measurement. Along with each series of measurements was carried a blank or control experiment which was made use of in calculating the per cent of adsorption.

EXPERIMENTAL RESULTS

1. Time of shaking

To find how long a shaking period was necessary to establish adsorption equilibrium, an experiment in which the time of shaking varied was carried out. The results are given in table 1.

From the figures in table 1 it is evident that a shaking period of 30 minutes is ample to establish equilibrium. In the following work, solutions were shaken for 45 minutes.

2. *Change in surface of adsorbent*

In table 2 are given the results of a series of measurements in which the amount of bromide ion and thorium B is the same but the weight of the silver bromide powder is changed. It is evident from table 2 that ordinary errors in weighing would not appreciably affect the percentage of thorium B adsorbed. Thus if the adsorbent were weighed only to the nearest milligram, the error in the per cent of thorium B adsorbed would not exceed 0.07.

TABLE 1

Time of shaking necessary to establish adsorption equilibrium

0.5 g. of silver bromide; 5 cc. of 0.04 *N* potassium bromide; 10 cc. of water; 10 cc. of nitric acid solution of thorium B

TIME OF SHAKING	CORRECTED ACTIVITY	ADSORPTION
minutes	*scale divisions per minute*	*per cent*
Control	39.0	
Control	39.5	
30	13.8	64.9
30	14.0	64.3
60	13.6	65.3
60	13.9	64.5
90	14.2	63.9
90	13.7	65.1

TABLE 2

WEIGHT OF SILVER BROMIDE	ACTIVITY	ADSORPTION
grams	*scale divisions per minute*	*per cent*
Control	76.2	
Control	77.7	
0.450	29.8	61.4
0.450	29.7	61.5
0.500	27.7	64.0
0.500	27.1	63.5
0.550	24.9	67.6
0.550	24.3	68.4

3. *Effect of light on the adsorption*

Five-tenths of a gram samples of silver bromide were used. Samples 3 and 4 in table 3 were handled in the dark room. Samples 5 and 6 were exposed to indirect sunlight for 10 minutes. All other conditions were the same as in previous experiments. We note that an exposure to white light effects our results but slightly. To eliminate errors from this source, however, all operations in the following work, except the final evaporation of the radioactive samples, were carried out in the dark room, using Eastman safelights for illumination.

TABLE 3

Effect of light on the adsorption

	ACTIVITY	ADSORPTION	AVERAGE
	scale divisions per minute	*per cent*	
Control	99.7		
Control	100.0		
Dark	44.7	55.2	54.7
Dark	45.7	54.2	
Light	43.1	56.8	56.9
Light	42.9	57.0	

TABLE 4

The "holding back" effect of lithium bromide

Concentration of nitric acid = 4 millimoles per liter

SILVER BROMIDE	CONCENTRATION OF LITHIUM BROMIDE	CORRECTED ACTIVITY	APPARENT PER CENT ADSORPTION	PER CENT OF ACTIVITY HELD BACK BY LITHIUM BROMIDE	CORRECTED PER CENT ADSORPTION
gram	*millimoles per liter*	*scale divisions per minute*			
0	0	96.5			
0	0	96.5			
0	0	95.5			
0.5	0	91.3	5.1		5.1
0	8	94.8		1.5	
0.5	8	29.8	69.0		67.5
0	20	94.3		2.0	
0.5	20	20.8	78.4		76.4
0	28	92.0		4.4	
0.5	28	18.2	81.1		76.7
0	40	89.1		7.4	
0.5	40	15.3	84.1		76.7
0	48	87.5		9.0	
0.5	48	13.5	86.0		77.0
0	60	84.2		12.5	
0.5	60.2	12.2	87.3		74.8

4. The "holding back" effect of lithium bromide

Lithium bromide is so hygroscopic that it took up water from the air before the measurements of the activity of the watch glasses containing the active material could be made. In table 4 are given the results using an excess of lithium bromide. In a similar experiment with the other alkali bromides, no "holding back" effect was observed at concentrations of 8 and 16 millimoles per liter. Accordingly, no corrections for this effect were necessary at these concentrations except in the case of lithium bromide.[1]

5. The effect of varying concentrations of thorium B on the adsorption

A study was made of the change of adsorption with a change in the activity of solution. The results are tabulated in table 5. These results, which indicate that the per cent adsorption decreases in solutions of higher ThB^{++} concentration, are in agreement with the general adsorption rule.

TABLE 5

The adsorption of thorium B on silver bromide with varying concentrations of thorium B

0.5 g. of silver bromide; concentration of nitric acid = 6 millimoles per liter; concentration of potassium bromide = 20 millimoles per liter

ACTIVE SOLUTION	CORRECTED ACTIVITY	ADSORPTION	AVERAGE
cc.	*scale divisions per minute*	*per cent*	
5 (Blank)	31.6		
5 (Blank)	31.3		
5	11.5	63.4	63.4
5	11.5	63.4	
10 (Blank)	64.4		
10 (Blank)	64.6		
10	26.6	58.8	59.1
10	26.2	59.4	
15 (Blank)	96.8		
15 (Blank)	96.2		
15	43.5	55.0	55.6
15	42.3	56.2	

6. The effect of hydrogen-ion concentration

A study was made of the effect of different hydrogen-ion concentrations in order to find out what concentration of hydrogen ion would give reproducible adsorptions of thorium B. The data is given in table 6.

It is evident that reproducible results are not obtainable in solutions in which the acid concentration is much less than 4 millimoles per liter. For a discussion of the factors involved, see King and Pine (1). In the

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[1] Professor Fajans, who is now investigating the cation effect in his laboratory in Munich, in a private communication (September, 1933) stresses the possibility of the introduction of an error in such work by what he calls the "crust effect." He gives his method for the elimination of such an error. In all our work attention was given to the formation of the salt crust on the watch glasses used for the activity measurements as described in the paper of King and Pine (reference 1). Where this error was greater than the experimental error, we have corrected for it by means of a control in which the halide salt was used without the silver bromide powder and the same careful evaporation was carried out.

following work, the acid concentration in the solutions investigated was held at 4 millimoles per liter.

TABLE 6

Effect of hydrogen-ion concentration on the adsorption of thorium B

0.5 g. of silver bromide; concentration of potassium bromide = 4 millimoles per liter

CONCENTRATION OF NITRIC ACID	CORRECTED ACTIVITY	ADSORPTION
millimoles per liter	*scale divisions per minute*	*per cent*
1	146.8	Blank
1	146.8	Blank
1	104.9	28.5
1	126.0	14.2
2	72.5	50.6
2	66.2	54.9
3	78.0	46.9
3	90.9	55.9
4	66.6	54.6
4	68.6	53.3
5	70.3	52.1
5	69.6	52.6
8	77.6	47.1
8	74.4	49.3

TABLE 7

The adsorption of thorium B on silver bromide in the presence of excess sodium bromide and potassium bromide

0.5 g. of silver bromide; concentration of nitric acid = 4 millimoles per liter

CONCENTRATION		CORRECTED ACTIVITY	ADSORPTION
millimoles per liter		*scale divisions per minute*	*per cent*
NaBr	0 (Blank)	71.5	
	0	70.3	1.67
	8	27.0	62.2
	20	17.4	75.7
	28	15.3	78.6
	40	14.2	80.1
	48	12.7	82.2
	60	10.8	84.9
KBr	0 (Blank)	74.9	
	0	72.1	3.7
	8	39.0	47.9
	20	25.0	66.6
	28	22.3	70.1
	40	18.5	75.3
	48	16.9	77.3
	60	16.8	77.5

7. *The adsorption of thorium B on silver bromide in the presence of varying concentrations of potassium bromide and sodium bromide*

The measurements were made over a large range in concentration of the two alkali bromides. The results are given in table 7.

TABLE 8

Adsorption of thorium B on silver bromide in the presence of excess of the alkali bromides

0.5 g. of silver bromide; concentration of nitric acid = 4 millimoles per liter

CONCENTRATION OF ALKALI BROMIDE	CORRECTED ACTIVITY	ADSORPTION	AVERAGE
millimoles per liter	*scale divisions per minute*	*per cent*	
LiBr 8	56.6	Blank	
8	56.2	Blank	
8	15.2	73.2	73.3
8	15.0	73.4	
16	53.8	Blank	
16	54.3	Blank	
16	11.5	78.6	78.1
16	12.1	77.6	
NaBr 8	16.3	70.0	70.8
8	15.4	71.7	
16	12.8	76.6	76.3
16	13.0	76.1	
KBr 8	55.0	Blank	
8	54.0	Blank	
8	22.4	58.9	61.0
8	20.1	63.2	
16	17.7	67.5	67.1
16	18.1	66.8	
RbBr 8	24.6	54.9	53.8
8	25.8	52.7	
16	20.8	61.8	62.4
16	21.1	63.1	
CsBr 8	33.4	38.7	38.7
8	33.3	38.8	
16	29.1	46.6	47.1
16	28.6	47.6	

8. *A study of the effect on the adsorption of all the different alkali bromides a concentrations of 8 and 16 mollimoles per liter*

The results are given in table 8 and plotted in the curves in figure 1.

8a. The effect on adsorption of lithium bromide and cesium bromide at concentrations of 0.1 and 0.01 millimoles per liter

The data in table 8 represent the results of a study of the adsorption of ThB^{++} on silver bromide in the presence of all the different alkali bromides at concentrations of 8 and 16 millimoles per liter. In table 8a, the results obtained with lithium bromide and cesium bromide at concentrations of 0.1 and 0.01 millimole per liter are given. These results are plotted in the graph of figure 1.

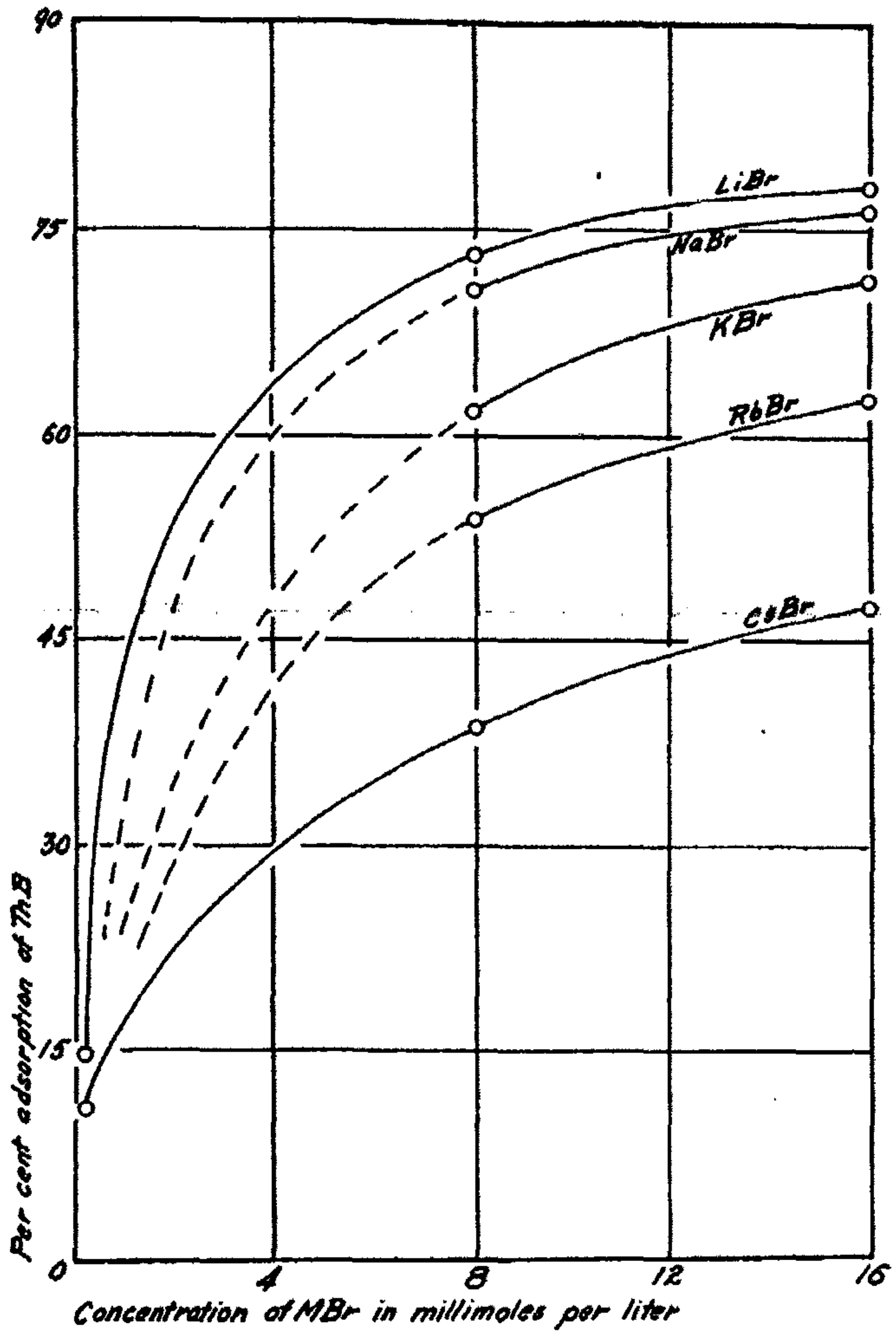

FIG. 1. ADSORPTION OF THORIUM B ON SILVER BROMIDE IN THE PRESENCE OF EXCESS OF THE DIFFERENT ALKALI BROMIDES

TABLE 8a

Adsorption of thorium B on silver bromide in the presence of excess of alkali bromide

0.5 g. of silver bromide; concentration of nitric acid = 4 millimoles per liter

CONCENTRATION OF ALKALI BROMIDE		CORRECTED ACTIVITY	ADSORPTION	AVERAGE
	millimoles per liter	*scale divisions per minute*	*per cent*	
CsBr	0.1	88.8	Blank	
	0.1	89.1	Blank	
	0.1	82.4	7.2	10.8
	0.1	75.9	14.5	
	0.01	85.5	3.7	3.1
	0.01	86.6	2.5	
LiBr	0.1	89.0	Blank	
	0.1	88.3	Blank	
	0.1	76.7	13.6	14.8
	0.1	74.5	16.1	
	0.01	85.1	4.2	3.5
	0.01	86.3	2.8	

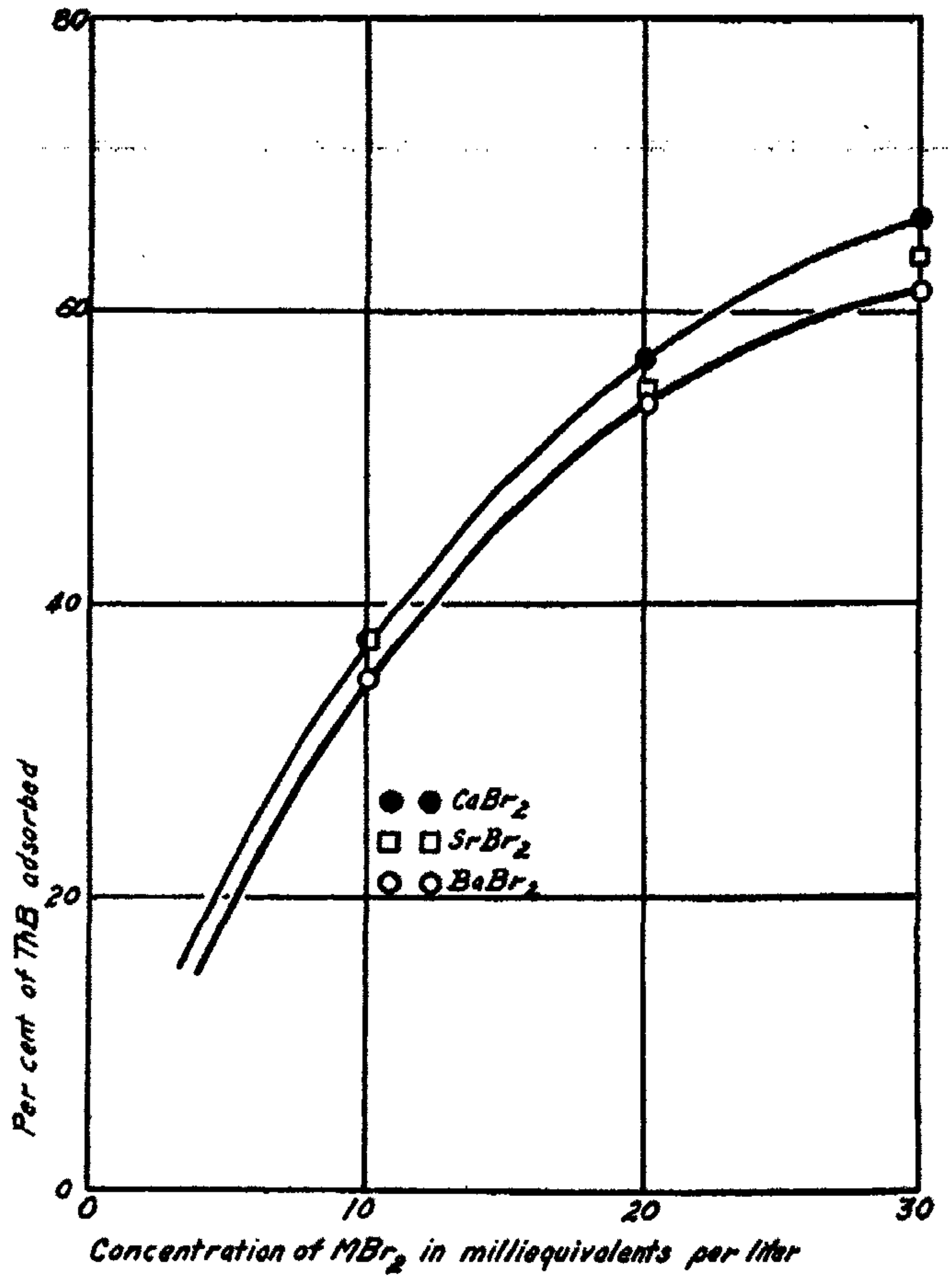

FIG. 2. ADSORPTION OF THORIUM B ON SILVER BROMIDE IN THE PRESENCE OF EXCESS OF ALKALINE EARTH BROMIDES

9. A study of the effect of the alkaline earth bromides on the adsorption of thorium B by silver bromide

Because of their hygroscopic properties in all cases a correction was made for the "holding back" effect. The results are given in table 9 and are plotted in the curves in figure 2.

TABLE 9

Effect of the alkaline earth bromides on the adsorption of thorium B on silver bromide

0.5 g. of silver bromide; concentration of nitric acid = 4 millimoles per liter

CONCENTRATION OF BROMIDE		CORRECTED ACTIVITY	ADSORPTION
milliequivalents per liter		*scale divisions per minute*	*per cent*
$CaBr_2$	30 (Blank)	77.3	
	10	48.5	37.3
	20	35.7	53.8
	30	26.1	66.2
$BaBr_2$	30 (Blank)	82.6	
	10	51.9	37.2
	20	37.4	54.7
	30	30.0	63.7
$SrBr_2$	30 (Blank)	83.1	
	10	54.6	34.3
	20	36.1	56.6
	30	32.1	61.4

DISCUSSION

In experiment 7 (table 7) the adsorption of thorium B on $AgBrBr^-$ particles was measured over a range of concentrations of excess sodium bromide and potassium bromide of from 8 millimoles to 60 millimoles per liter. The adsorption of thorium B is greater for sodium bromide than for potassium bromide throughout the whole range.

In experiments 8 and 9 data were obtained for lithium bromide, sodium bromide, potassium bromide, rubidium bromide and cesium bromide. The order for the repression of the adsorption of thorium B is $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ at all concentrations measured. At the very low concentration of 0.01 millimole per liter, the differences observed may be attributed to experimental error.

In experiment 9 (table 9, figure 2), the effects of the three alkaline earth bromides—barium bromide, calcium bromide, and strontium bromide—were measured. There is a very small difference, if any, in the effect of the alkaline earth ions on the adsorption of thorium B by silver bromide.

Since in all of the many series of measurements carried out, all factors were held constant with the exception of the cation to be found in the system at equilibrium, there must be some connection between the order of adsorption and some properties of these cations. We may look on the phenomenon as silver bromide particles negatively charged by the addition of bromide ions selectively adsorbing thorium B from solutions containing the same concentrations of the different alkali and alkaline earth cations. Because thorium B forms a much more insoluble compound with the oppositely charged ion of the silver bromide–bromide particles than do the alkali and alkaline earth ions, it will be much more readily adsorbed. However it has been shown that hydrogen ion, which forms no insoluble compound, may displace the very easily adsorbed ThB^{++} ions from the surface of crystals. It can be expected that all cations behave in some such way. In other words, all ions possess some tendency to be fixed to a polar crystal surface. Therefore, we may use the above data to arrange the cations in the order of their adsorbability on the silver bromide–bromide particles.

TABLE 10

ALKALI ION	PER CENT ADSORPTION OF THORIUM B	HEATS OF HYDRATION	SOLUBILITIES AT 25°C.	IONIC SIZE
		calories per gram	*moles per 100 g. water*	*A. U.*
Li^+	73.3	120	2.09	0.70
Na^+	70.8	92	0.814	1.00
K^+	61.0	72	0.569	1.33
Rb^+	53.8	68	0.695	1.52
Cs^+	38.7	62	0.578	1.70

According to the adsorption theories mentioned in the previous papers, (1) that cation which forms the most insoluble compound will be most easily adsorbed, (2) that cation which is most easily deformable will be most easily adsorbed, and (3) that cation which is least hydrated will be most easily adsorbed. In the first column of table 10 are given the alkali ions in order of their adsorbability as measured by the per cent of thorium B ions adsorbed in 8 millimoles per liter of alkali bromide; in the second column are given the heats of hydration of these cations in calories per gram, which can be used as a measure of the hydration of the ions; in the third column are given the solubilities of the alkali bromides in moles per 100 g. of water at 25°C; in the fourth column are given the sizes of the cations in Ångström units (6).

Fajans (7) has measured the molecular refractivities of the alkali ions to show their deformability. The deformability is in accord with the size, the largest ion being the most easily deformed or polarized in forming a compound.

SUMMARY

1. A study has been made of the adsorption of thorium B ions on silver bromide crystals in the presence of various concentrations of the alkali and alkaline earth bromides.

2. It has been shown that when the bromide ion concentration has been kept constant and the cation has been changed there has been a change in the adsorption of the thorium B ions on the silver bromide crystals due to an adsorption of the cations along with the thorium B ions.

3. There appears to be a relation between the adsorbability of the cations and their heats of hydration, their ionic size and the solubility of their bromide salts.

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THE COLORS OF THE COPPER SALTS

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INTRODUCTION

In 1892 Ostwald (1) pointed out that according to the electrolytic dissociation theory the absorption spectrum of a dilute salt solution must depend exclusively on the absorption spectrum of the solvent, the cation, and the anion. From this it follows that we shall have identical absorption spectra for dilute solutions of different salts with the same colored ion. In accordance with this, dilute solutions of copper sulfate, nitrate, chloride, and bromide should have the same blue color, and it is an experimental fact that they do. The undissociated salt may have a different color and Ostwald called attention to the fact that anhydrous cupric chloride is yellowish-brown, cupric bromide blackish-violet and cupric sulfate gray. Since nobody was especially interested in those days in hydrated ions, the behavior of the copper salts was taken to mean that the copper ion is blue. We see now that that is not necessarily true. All that the experiments really show is that the copper ion common to, and occurring in, those dilute solutions is blue.

Nobody paid any attention at that time to the earlier observation by Vogel (2) that "copper sulphate is one of the few substances which shows the same absorption spectrum in the solid state and in solution. It absorbs the red very strongly up to wave length 620; from there on the absorption decreases rapidly and ends in the yellow-green. Green, bright blue, and dark blue are practically not absorbed, but there is some absorption in the violet."

Since 1908 Hantzsch (3) has taken the ground that there is no necessary relation between color and ionization. He states that colored substances are those which contain an element or group capable of forming a complex of the Werner type. If the complex is saturated completely, all the coördination places being filled, then the color is constant, regardless of the conditions surrounding the complex. Dissociation, salt formation, solution, change of temperature or of solvent, will have no effect on the color. Conversely, if a given color persists through the changing of such conditions, we may regard the saturated complex as persisting through the changes. For those complex states which may not be entirely saturated but become so through a change in conditions, we shall expect an accompanying change in color. If, by any dehydration or substitution, the complex is altered, this will also result in a change of color. Anhydrous salts, which are unsaturated but which become saturated by the addition of water or ammonia molecules or other groups, will change color until complete saturation is reached. After this point there will be no further change in color. If a saturated complex cannot be isolated as a solid or is stable only in presence of a large excess of the solvent, there may be intermediate complexes which will explain the color of certain solutions.

From a study of the chloroplatinate salts of the alkalies, Hantzsch concluded that neither change of dissociation nor change of temperature had any effect on the color. Change of solvent had only a slight effect. An investigation of chromate solutions (4) showed that the acid and its potassium salt had identical absorption, which was independent of dilution and of temperature change. Addition of sulfuric acid up to 10 normal had only a slight effect, accounted for by the formation of some $H_2Cr_3O_{10}$. Solutions of chromic acid in water, alkalies, and methyl alcohol were optically identical in all dilutions examined, except in the water solutions where the slight variation was accounted for by some dichromate ion. The dichromate and chromate solutions were of course unlike. Hantzsch states that the color group of the acid solution is the complex Cr_2O_7, and of the chromate solution CrO_4, irrespective of whether these groups are joined to hydrogen or to an alkali metal. The degree of electrolytic dissociation has no effect on the color because the color of the ion is the same as that of the undissociated complex.

Hantzsch points out that, years before, Sabatier (5) had found that "the absorption exercised by potassium dichromate dissolved or solid is practically the same as that produced by the chromic acid in the salt."

In a study of alkali permanganates Hantzsch and Clark (6) confirmed these assumptions. Change of temperature or of alkali metal had no effect and the effect of adding sulfuric acid was but small. There was no effect due to change of concentration and the slight effect produced by change of solvent was due to a partial reduction of the permanganates. Hantzsch found that the absorption of solid copper sulfate pentahydrate was very similar to that of its aqueous solution, thus confirming to that extent the earlier observation by Vogel. Hantzsch concluded that the color of both ions is due to the complex, $Cu \cdot 4H_2O$. He believed that this group is also present in dilute solutions of cupric chloride, while the green concentrated solutions contain the unsaturated complex, $Cu \cdot 2H_2O$, which is also present in the solid hydrated salt.

Hantzsch ascribes the intense blue color of the copper ammines to the saturated complex, $Cu \cdot 4NH_3$. Investigation of the copper ammines by Hantzsch and Robertson (7) showed the color to be independent of the anions. The same was true for pyridine solutions, but the complex is apparently less stable in the pyridine solutions, as more is required to produce the blue color. Hantzsch suggests the presence of such groups as $Cu \cdot 3Py \cdot H_2O$ or $Cu \cdot 2Py \cdot 2H_2O$, as being likely. In the case of both solid and solution the saturated complex is the chromophoric group, such as $Cu \cdot 4H_2O$ or $Cu \cdot 4NH_3$. This chromophoric group determines the color regardless of the degree of electrolytic dissociation of the compound in which it appears.

Some of Hantzsch's conclusions had been reached independently and somewhat earlier by Bjerrum (8). "I will next emphasize that it is permissible to assume that the ions of an electrolyte have the same color whether in the free or the bound state, so long as no new complex is formed. This assumption was put forward by me as probable in the spring of 1907 (9). I came to this conclusion by combining the optical data now being presented with the newer views on the constitution of inorganic salts. In the fall of 1907 Hantzsch formulated the same generalization and confirmed it by new experimental data. Just recently some studies on the color of the chromic salts has given me a very good confirmation of this law. I propose to discuss these investigations more fully elsewhere and I will only mention the following here. All normal hexaquochromic salts have exactly the same color, the color of the hexaquochromic ion, even at concentrations at which the salts are only very slightly dissociated into ions."

A possible explanation of the practical identity of color of crystallized copper sulfate pentahydrate and of copper sulfate solutions is given by the theory of complete dissociation. If copper sulfate is 100 per cent ionized under all conditions, there is no reason for any change in color with changing concentration. The difficulty with this is that the monohydrate, $CuSO_4 \cdot H_2O$, is green and the anhydrous copper sulfate is colorless. From this it follows that either anhydrous copper sulfate is not dissociated at all or that the copper ion is not blue.

Roscoe and Schorlemmer (10) state that when copper sulfate pentahydrate or trihydrate is heated for some time to 100°C., the monohydrate, $CuSO_4 \cdot H_2O$, remains as a bluish-white powder. This is not correct. It was known at least a century ago that monohydrated copper sulfate is green. Graham (11) says that "the sulphate of copper with one atom [molecule] of water was also obtained in a crystallized state by Dr. Thomson and called by him green sulphate of copper." Müller (12) found that the monohydrate is greenish, and we have confirmed his results. Müller looks upon the green color of the monohydrate and the lack of color of the anhydrous sulfate as quite inexplicable.

SPECIAL ASSUMPTIONS

We adopt the general theory of Hantzsch; but the facts now at our disposal make necessary some minor changes in the wording. For instance, the experiments of Dewar (13) show that apparently all colored substances become paler with falling temperature. "The optical properties of bodies cooled to the temperature of boiling liquid air will require long and patient investigation. An interesting fact, easily observed, is the marked change in colour of various bodies. Thus, for instance, oxide, sulphide, iodide of mercury, bichromate of potash, all become yellow or orange; while nitrate of uranium and the double chloride of platinum and ammonium become white. Chromic acid, dilute solutions of iodine in alcohol, strong solutions of ferric chloride and other coloured solutions become greatly changed. Such facts are sufficient to prove that the specific absorption of many substances undergoes great changes at the temperature of −190°C."

When the change with falling temperature involves an apparent change from yellow to white, as is the case with heated zinc oxide, this could easily be considered as contradicting the wording of Hantzsch's theory even though it does not violate the real principle, because the change is only or chiefly one of intensity. In the discussion of the colors of the cupric salts, so far as affected by water and ammonia, we make the following assumptions:—

1. The color of the chromophoric group does not vary appreciably with varying degree of ionization.
2. The color of the chromophoric group becomes paler with falling temperature.
3. The anhydrous cupric ion is not blue. It is probably colorless; but the possibility of its being red is not yet excluded.
4. Cupric copper with one or two molecules of water attached is green.
5. Cupric copper with three or more molecules of water attached is blue.
6. The NH_3 group has an effect similar to that of a water molecule in the copper complex, though the actual blue is different.
7. Copper oxide is blue and not black.
8. Some double salts have an effect which cannot be predicted at present, anhydrous potassium copper sulfate being blue.

GREEN AND BLUE SALTS

Anhydrous cupric sulfate, fluoride, selenate, and perrhenate are colorless. Anhydrous cupric nitrate has been reported by Ditte (14) as nearly colorless, though with a slight greenish tint. It is probable that this discoloration is due to incomplete drying or to slight decomposition, and that the pure anhydrous nitrate is colorless like the other salts cited. If these salts are ionized appreciably, then the anhydrous cupric ion is colorless. If the salts are not ionized appreciably, cupric copper in this form is colorless. We thought, at first, that Hantzsch's theory required that anhydrous cupric ion should be colorless, but there are some anhydrous copper double salts which are red. It would follow equally well from this that anhydrous cupric ion is red. Until we know whether the red or the colorless salts contain the simple cupric group, the question of the color of the anhydrous cupric ion must remain undecided. We shall discuss the question more in detail when considering the brown and red salts. The important thing from our point of view is that the blue ion in hydrated copper sulfate and nitrate cannot be the anhydrous cupric ion.

TABLE 1

Green salts

$\mathrm{CuSO_4 \cdot H_2O}$
$\mathrm{CuSO_4 \cdot 2NH_3}$
$\mathrm{CuSO_4 \cdot NH_2OH}$
$\mathrm{CuSeO_4 \cdot 2NH_3}$
$\mathrm{CuSeO_3 \cdot NH_3}$
$\mathrm{CuSeO_3 \cdot NH_3 \cdot H_2O}$
$\mathrm{CuWO_4 \cdot 2H_2O}$
$\mathrm{CuCl_2 \cdot 2H_2O}$
$\mathrm{CuCl_2 \cdot 2NH_3}$
$\mathrm{CuBr_2 \cdot 2NH_3}$
$\mathrm{CuI_2 \cdot 2NH_3}$
$\mathrm{CuC_2O_4 \cdot NH_3}$
$\mathrm{Cu(CH_3CO_2)_2 \cdot NH_3}$
$\mathrm{Cu(CH_3CO_2)_2 \cdot C_5H_5N}$
$\mathrm{Cu(CCl_3CO_2)_2 \cdot 2H_2O}$
$\mathrm{CuCl_2 \cdot 2KCl \cdot 2H_2O}$
$\mathrm{CuBr_2 \cdot 2NH_4Br \cdot 2H_2O}$

TABLE 2

Blue salts

$\mathrm{CuSO_4 \cdot 3H_2O}$
$\mathrm{CuSO_4 \cdot 5H_2O}$
$\mathrm{CuSO_4 \cdot 4NH_3}$
$\mathrm{CuSO_4 \cdot 5NH_3}$
$\mathrm{CuSO_4 \cdot 4NH_3 \cdot H_2O}$
$\mathrm{CuSO_4 \cdot 5NH_2OH}$
$\mathrm{CuSeO_4 \cdot 3H_2O}$
$\mathrm{CuSeO_4 \cdot 5H_2O}$
$\mathrm{CuSeO_4 \cdot 5NH_3}$
$\mathrm{CuSeO_3 \cdot 3NH_3}$
$\mathrm{CuSeO_3 \cdot 2NH_3 \cdot H_2O}$
$\mathrm{Cu(ReO_4)_2 \cdot 4H_2O}$
$\mathrm{Cu(ReO_4)_2 \cdot 4NH_3}$
$\mathrm{Cu(NO_3)_2 \cdot 3H_2O}$
$\mathrm{Cu(NO_3)_2 \cdot 6H_2O}$
$\mathrm{Cu(NO_3)_2 \cdot 4NH_3}$
$\mathrm{Cu(NO_3)_2 \cdot 6NH_3}$
$\mathrm{Cu(NO_2)_2 \cdot 4NH_3}$
$\mathrm{CuWO_4 \cdot 4NH_3}$
$\mathrm{CuMoO_4 \cdot 2NH_3 \cdot H_2O}$
$\mathrm{CuSiF_6 \cdot 6H_2O}$
$\mathrm{CuCl_2 \cdot 4NH_3}$
$\mathrm{CuCl_2 \cdot 6NH_3}$
$\mathrm{Cu(ClO_3)_2 \cdot 4H_2O}$
$\mathrm{Cu(ClO_3)_2 \cdot 6H_2O}$
$\mathrm{Cu(ClO_3)_2 \cdot 4NH_3}$
$\mathrm{Cu(ClO_3)_2 \cdot 6NH_3}$
$\mathrm{CuBr_2 \cdot 5NH_3}$
$\mathrm{CuBr_2 \cdot 6NH_3}$
$\mathrm{Cu(BrO_3)_2 \cdot 4NH_3}$
$\mathrm{CuI_2 \cdot 5NH_3}$
$\mathrm{CuI_2 \cdot 6NH_3}$
$\mathrm{CuI_2 \cdot 4NH_3 \cdot H_2O}$
$\mathrm{Cu(IO_3)_2 \cdot 4NH_3}$
$\mathrm{Cu(IO_3)_2 \cdot 4NH_3 \cdot H_2O}$
$\mathrm{Cu(CNS)_2 \cdot 4NH_3}$
$\mathrm{Cu(CNS)_2 \cdot 5NH_3}$
$\mathrm{Cu(CNS)_2 \cdot 6NH_3}$
$\mathrm{CuSO_4 \cdot M_2SO_4 \cdot 6H_2O}$*
$\mathrm{Cu(C_2O_4) \cdot 5NH_3}$
$\mathrm{CuC_2O_4 \cdot 2NH_3 \cdot H_2O}$
$\mathrm{Cu(HCO_2)_2 \cdot 4NH_3}$
$\mathrm{Cu(HCO_2)_2 \cdot 2C_6H_5N \cdot H_2O}$
$\mathrm{Cu(CH_3CO_2)_2 \cdot 4NH_3}$
$\mathrm{Cu(CH_3CO_2)_2 \cdot 4C_6H_5N}$

* M is K, Rb, Cs, $\mathrm{NH_4}$.

In table 1 is given a list of some cupric salts which are green when crystallizing with one or two molecules of water, ammonia, hydroxylamine, or pyridine. The list is not exhaustive.

The free acids and the sodium salts of the acids in table 1 are colorless, whether hydrated or not, so that there is no reason to believe that the water or ammonia influences the color by being attached to the anion. Where the literature was conflicting as to the color, the salts have been made. Unless the color was perfectly obvious, the crystals were immersed in a liquid of approximately the same index of refraction to eliminate diffuse reflection. The color was then checked by several observers.

In table 2 is given a list of some of the blue cupric salts with three or more molecules of water, ammonia, hydroxylamine, or pyridine.

Chuard (15) claims to have obtained a blue cupric chloride with three molecules of water by working below zero. This would be a welcome confirmation of the theory, but no one else has yet been able to isolate this hydrate. A conspicuous exception to the assumption that cupric salts with three or more molecules of water are blue is $CuCl_2 \cdot CdCl_2 \cdot 4H_2O$, a green salt. We know that cadmium salts in general tend to be hydrated, so that it is probable that part of the water in the crystal is attached to the cadmium, and that the formula should be written $CuCl_2 \cdot 2H_2O \cdot CdCl_2 \cdot 2H_2O$. When the red crystal, $CuCl_2 \cdot LiCl \cdot 2H_2O$, is discussed later, it will be shown that some of the water is undoubtedly attached to the lithium.

BROWN AND RED SALTS

Hantzsch's theory enables us to draw some interesting conclusions in regard to some of the brown and red cupric salts. Anhydrous cupric chloride is a yellow-brown; but Bancroft and Weiser (16) reported that its vapor is violet-red. This has been confirmed by volatilizing the anhydrous chloride rapidly either by itself or in an atmosphere of chlorine to prevent dissociation. In both cases the vapors were distinctly violet-red and condensed to the brown solid. From Hantzsch's theory it follows that the vapor must have a different constitution from the solid. Viard (17) has already shown that cupric chloride and cupric bromide are abnormal, because addition of an excess of concentrated sulfuric acid precipitates anhydrous yellow-brown cupric chloride and anhydrous black cupric bromide, respectively, instead of converting these salts into sulfates. Hantzsch and Carlson (18) state quite definitely that cupric chloride is a pseudo salt.

Qualitatively, solid anhydrous cupric chloride is similar in color to one constituent of a solution of cupric chloride in aqueous hydrochloric acid. Donnan and Bassett (19) showed that the yellow-brown color in these solutions is due to an anion containing copper, $CuCl_3$ or something of that type. Kohlschütter (20) extended the work of Donnan and Bassett, and found that a brown color moved to the anode in concentrated solutions of cupric chloride. In a dilute solution all the copper went to the cathode, but increase of concentration caused some and then more copper to go to the anode. On these facts we conclude that anhydrous cupric chloride is really the copper salt of a chlorocupric acid, and that the formula should be written $Cu(CuCl_4)$ or $Cu(CuCl_3)_2$.

On the other hand, some of the anhydrous double salts are red, such as $CuCl_2 \cdot NH_4Cl$, $CuCl_2 \cdot CsCl$, and $CuCl_2 \cdot KCl$. In these salts we undoubtedly have the cupric chloride having the same chromophoric group as the vapor. It is probable that an x-ray analysis would show a distinct difference between the copper atoms in anhydrous cupric sulfate and those in anhydrous potassium cupric chloride. This is the more plausible because Hendricks and Dickinson (21) have examined some of the hydrated double chlorides and have found evidence indicating a $CuCl_2 \cdot 2H_2O$ group in the ammonium, potassium, and rubidium salts of this type. This confirms our application of Hantzsch's theory. It is a pity that Hendricks and Dickinson did not also study the salt which we write $CuCl_2 \cdot 2H_2O \cdot CdCl_2.2H_2O$.

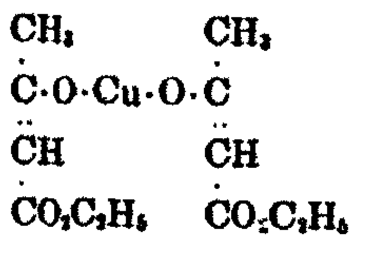
The hydrated double salt of lithium and copper chlorides has the composition, $CuCl_2 \cdot LiCl \cdot 2H_2O$, and is red. Consequently the water must be attached to the lithium chloride and not to the cupric chloride. This is additional evidence for the formula which we have given for hydrated copper cadmium chloride and should be confirmed by an x-ray study.

Engel (22) and Sabatier (23) have made a red compound of cupric chloride, hydrogen chloride, and water. Engel wrote the formula $CuCl_2 \cdot HCl \cdot 3H_2O$ and considered that the compound was derived from the hypothetical trihydrate of cupric chloride. Sabatier wrote the formula $CuCl_2 \cdot 2HCl \cdot 5H_2O$ and did not care how it came to pass. Since neither man had a method of analysis that was worth anything, nobody knows what the composition really was; but the color was red—Sabatier called it a hyacinth red—and changed reversibly from red to green and back again as hydrogen chloride (and water) evaporated off and was put back again.

With the idea of testing Hantzsch's conclusions, anhydrous cupric chloride was added to molten potassium chloride and to molten sodium chloride. In both cases the melt was at once colored red. In time the melt decolorized, presumably owing to volatilization of the cupric chloride. This agrees with what Hantzsch would predict if the cupric chloride vapor is normal, and means apparently that anhydrous cupric ion is red. This contradicts the conclusion drawn from the colorless anhydrous salt. Either copper sulfate, fluoride, selenate, nitrate, and perrhenate form colorless complexes in which copper is not the basic radical, or copper is not the basic radical in cupric chloride vapor. Until some independent evidence is forthcoming, it is impossible to determine which conclusion is right.

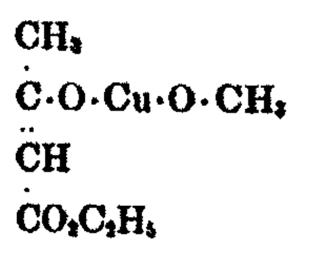
On general principles it seems probable that cupric sulfate and cupric nitrate are normal and not pseudo salts. There is no reason why the vapor of cupric chloride should not be abnormal to some extent. We know that it condenses to a pseudo salt. Sabatier (24) found that cupric bromide is yellowish-red in absolute alcohol and is purple in concentrated solutions of hydrobromic acid, potassium bromide, sodium bromide, lithium bromide, and calcium bromide. There are anhydrous double salts which are red, but apparently no single salts. According to Bödtker (25) anhydrous cupric chloride in absolute alcohol is brown, although the salt which crystallizes is green and has the composition $CuCl_2 \cdot 2CH_3CH_2OH$.

The organic cupric compounds are blue, green, or brown, but apparently never red. Copper acetylacetonate (26) is cobalt-blue when anhydrous and sky-blue when crystallizing with two molecules of water. Copper acetoacetic ethyl ester (27) is green, while the basic methylate is blue. Wislicenus wrote the formulas:



$$\begin{array}{ll} CH_3 & CH_3 \\ \dot{C}\cdot O\cdot Cu\cdot O\cdot \dot{C} & \\ \ddot{C}H & \ddot{C}H \\ \dot{C}O_2C_2H_5 & \dot{C}O_2C_2H_5 \end{array}$$

Copper acetoacetic ester
(green)



$$\begin{array}{l} CH_3 \\ \dot{C}\cdot O\cdot Cu\cdot O\cdot CH_3 \\ \ddot{C}H \\ \dot{C}O_2C_2H_5 \end{array}$$

Basic methylate
(blue)

The blue form is stable in methyl alcohol and the green form in benzene.

The copper derivative of benzoylcamphor (28) is greenish-yellow in alcohol and greenish-brown in chloroform. Since the red salts occur only under conditions where one would expect pseudo salts, we feel that it is probable that the violet-red of the cupric chloride vapor is abnormal and that the anhydrous cupric ion is colorless.

In fused ammonium acetate at 90°C. cupric chloride, sulfate, nitrate, chlorate, acetate, and oxide are blue, undoubtedly because of the formation of the $Cu(NH_3)_4$ group. In fused ammonium sulfate at 160°C. they are all green, undoubtedly because of the formation of the $Cu(NH_3)_2$ or $Cu(NH_3)$ group. In fused ammonium nitrate at 160°C. all were green except the acetate and oxide, which were blue. All the salts gave a black color in a fused mixture of potassium and sodium nitrates at 300°C. This is apparently due to the formation of undissolved, black, cupric oxide.

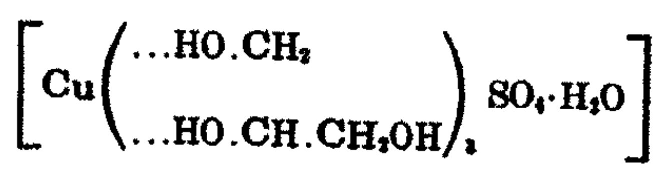
SOLUTIONS

Addition of considerable quantities of sulfuric acid to a copper sulfate solution causes the color to shift from blue to green. This is what should happen if the chromophoric group was being dehydrated.

Gladstone (29) says that "even where different salts of a base have the same colour, the same amount of the base does not give the same intensity of colour. Thus if equal portions of oxide of copper be dissolved respectively in acetic, hydrochloric, nitric, and sulphuric acids, and equally diluted, the acetate will be found to be far deeper in colour than the sulphate, and this again far deeper than the chloride. On being converted into ammoniacal salts, these four approximate more nearly, but are still far from identical in colour."

The acetate did not seem to be entirely trustworthy because of the possible presence of basic salt. Dr. F. H. Getman was kind enough to run spectrophotometric determinations on copper nitrate and copper sulfate solutions. He confirmed Gladstone's observations, finding that solutions of copper nitrate are a deeper blue than the equivalent solutions of copper sulfate. This does not apply of course to very dilute solutions. Since copper nitrate crystallizes with six molecules of water instead of with five, the natural hypothesis is that the copper in undissociated copper nitrate is more highly hydrated than the copper in the corresponding copper sulfate solutions. As yet there is no independent proof of this. We hoped to find in the literature that the solid solutions of copper and zinc sulfates containing seven molecules of water per molecule of salt were much bluer per unit of copper in a given thickness than the corresponding solid solutions with five molecules of water. The literature seems to destroy this hypothesis. Friend (30) says that copper sulfate forms pale blue monoclinic crystals of the series, $CuSO_4\cdot 7H_2O\cdot ZnSO_4\cdot 7H_2O$, but dark blue triclinic crystals of the series of solid solutions, $CuSO_4\cdot 5H_2O\cdot ZnSO_4\cdot 5H_2O$. This is so inherently improbable that we suspect that proper allowance has not been made for the low copper concentration. This point will be checked as soon as possible.

In the field of non-aqueous solutions the evidence is rather contradictory. Guthrie (31) heated glycerol with cupric sulfate, obtaining an emerald-green solution. This is what one would expect if there were dehydration. Grün and Bockisch (32) say that copper sulfate pentahydrate with dry glycerol gives a dark blue solution. On precipitation with alcohol they obtained a blue oil which could be dried to a blue glass. They write the formula for this:



$$\left[\mathrm{Cu}\left(\begin{matrix}\ldots\mathrm{HO.CH_2}\\ \ldots\mathrm{HO.CH.CH_2OH}\end{matrix}\right)_2 \mathrm{SO_4\cdot H_2O}\right]$$

On repeating Guthrie's experiments we got a green solution as he did. We were not using absolutely anhydrous glycerol any more than Guthrie was. It is possible, though not proved, that anhydrous glycerol gives a blue solution and glycerol with small amounts of water gives a green one.

As has been stated, cupric chloride gives a brown solution in absolute alcohol (33) and a green diethylate crystallizes from it. Ley (34) found cupric chloride to be green in alcohol and blue in pyridine. Mason and Mathews (35) reported both green and blue solutions in pyridine just as in water. They suggest that the green is due to cuprous chloride, as this salt is known to be green in pyridine; but this does not yet seem to be necessary. Sammis (36) found that both cupric acetate and cupric formate are blue in pyridine. Mathews and Benger (37) found only two stable solvates of cupric acetate and pyridine, a green one with one molecule of pyridine and a blue one with four molecules. Hantzsch and Robertson (38) state that all the cupric salts give the same blue in dilute solution in aqueous pyridine. They suggest that the blue complex may contain water as well as pyridine.

MISCELLANEOUS CASES

We are still in the descriptive stage with regard to the copper salts. It seems fairly certain that the addition of one or two molecules of water to the copper atom will give a green color, while the addition of three or more will give a blue color; but we do not know why the one is green and the other blue rather than two other colors. Consequently we cannot tell as yet what other grouping will make a copper compound green, blue, or red. The alkaline cupric tartrate solution contains a blue anion, but we could not have predicted that.

Covellite, cupric sulfide, is blue and so apparently is finely divided cupric oxide. In borate and silicate glasses cupric oxide is blue. Here there can be no question of hydrated ions, and the turning green of these glasses when heated too hot is due to the formation of cuprous oxide (39) and has nothing whatsoever to do with the green of such salts as hydrated cupric chloride.

Dioptase, H_2CuSiO_4, is green, and crysocolla, $H_2CuSiO_4 \cdot H_2O$, is blue. Egyptian blue (40) is crystallized $CaO \cdot CuO \cdot 4SiO_2$, and is blue. At 850–900°C. it changes reversibly to a green glass. This is undoubtedly due to the partial decomposition of the cupric salt, but this has not yet been shown analytically. It is possible, though not proved, that dioptase may contain some cuprous salt.

Copper pentammino metachloroantimonate, $Cu(SbCl_6)_2 \cdot 5NH_3$, is blue (41) as it should be, but it becomes green on losing ammonia and that could not have been predicted. The analyses of Scheele's green, Paris green, etc., are so conflicting (42) that one cannot tell anything about them; but copper metarsenite, $Cu(AsO_2)_2$, is said to be colorless and the dihydrated salt, $Cu(AsO_2)_2 \cdot 2H_2O$, is said to be green. That is satisfactory if true.

It is impossible to make any definite statement at present about the basic salts. Basic copper sulfate, $CuSO_4 \cdot 3CuO_2H_2$, is green (43) and $CuSO_4 \cdot CuO$ is said to be orange. Malachite, $CuCO_3 \cdot CuO_2H_2$, is green, and azurite, $2CuCO_3 \cdot CuO_2H_2$, is blue.

The double sulfate of potassium and copper is a very trying case. Cowan and Ferguson (44) say that the dihydrate, $K_2SO_4 \cdot CuSO_4 \cdot 2H_2O$, is bluer than the hexahydrate. The anhydrous salt is blue. One does not like to postulate that potassium sulfate is equivalent to three or more molecules of water in its chromophoric properties and yet Graham (45) put forward what is practically our working hypothesis nearly one hundred years ago. "This double salt [$K_2SO_4 \cdot CuSO_4$] retains its blue color after being fused at a red heat and cooled, and does not become white like the sulphate of copper. Indeed it appears that to be colored, the salts of the oxide of copper require the addition of some other constituent, such as saline water [what is now called water of crystallization], sulphate of potash, or ammonia. Hence if the absolute sulphate of copper could be obtained in a crystallized state [as has since been done], it would be a colorless salt."

A century of progress has brought us back to Graham. Our conclusions and those of Hantzsch would also be acceptable to Gladstone (46). "Every observation made on this salt [cupric chloride] is perfectly explicable on the supposition that the proper color of chloride of copper is brown, and that it forms hydrates which are green or blue, just as the white sulphate of copper becomes blue when hydrated. Some of the facts, too, are *more* easily explained on this view.

"Thus it is hard to imagine that if green be the color of CuCl [$CuCl_2$], and blue that of CuO, HCl [$CuO \cdot 2HCl \cdot H_2O$ or $CuO \cdot 2HCl$], the addition of more HCl should render it green; while it is readily conceivable that the hydrochloric acid should replace a portion of the water in the blue hydrated chloride of copper and form a green double chloride, CuCl, 2HCl [$CuCl_2 \cdot xHCl \cdot yH_2O$].

"If the change of color is to be taken as evidence that crystallized chloride of copper becomes, when treated with a considerable amount of water, CuO, HCl, a parity of reason should lead us to conclude that the bluish-green crystals contain none of the yellowish-brown CuCl [$CuCl_2$]; yet, if we suppose that these crystals actually contain the oxide, we can give no consistent account of the subsequent change of color on solution."

CONCLUSIONS

1. The cupric salts confirm Hantzsch's theory of the identity of color of solid, solution, and vapor when the chromophoric groups are the same in the three states. Conversely, a difference in the color connotes a difference in the chromophoric groups.
2. The color of a chromophoric group is practically independent of the degree of ionization but becomes less intense with falling temperature.
3. Cupric copper with one or two molecules of water is green; with three or more molecules of water it is blue.
4. The ammonia molecule has practically the same effect in a copper complex as has the water molecule, though the shade of the blue is different.
5. Anhydrous cupric sulfate, fluoride, selenate, nitrate, and perrhenate are colorless, which means that the anhydrous cupric ion is colorless if these salts are normal.
6. We have confirmed the statement by Bancroft and Weiser that cupric chloride vapor is red. If the vapor is normal, the theory of Hantzsch requires that the color of the anhydrous cupric ion is red. It is probable that the vapor contains a pseudo salt.

7. Anhydrous cupric chloride is yellow-brown, which is the color of the anion in aqueous hydrochloric acid solutions of cupric chloride and is not the color predicted by the theory of Hantzsch. Consequently anhydrous cupric chloride must contain copper as part of the acid radical. Hantzsch has himself pointed out that anhydrous cupric chloride must be a pseudo salt.

8. The anhydrous double salts, $CuCl_2 \cdot NH_4Cl$, $CuCl_2 \cdot CsCl$, and $CuCl_2 \cdot KCl$, are red, and the chromophoric groups are therefore similar to that in the vapor of cupric chloride.

9. The hydrated double chloride, $CuCl_2 \cdot LiCl \cdot 2H_2O$, is red and must therefore have the two molecules of water attached to the lithium chloride and not to the copper.

10. The hydrated salt, $CuCl_2 \cdot CdCl_2 \cdot 4H_2O$, is green and not blue. Its formula should therefore be written $CuCl_2 \cdot 2H_2O \cdot CdCl_2 \cdot 2H_2O$.

11. By means of x-ray analysis Hendricks and Dickinson have shown the probable existence of the group, $CuCl_2 \cdot 2H_2O$, in some of the green double salts. It is very much to be desired that a systematic study should be made.

12. The anhydrous cupric ion is probably colorless, but may possibly be red.

13. Copper produces a blue color in the borate and silicate glasses and in crystallized Egyptian blue.

14. We do not know why copper is green with one or two molecules of water and blue with three or more molecules of water and consequently we can not predict what other groupings will give blues, greens, or reds.

15. The basic salts are rather hopeless for the present.

16. The anhydrous double sulfate, $K_2SO_4 \cdot CuSO_4$, is blue. It was pointed out by Graham in 1835 that the effect of potassium sulfate is similar to that of water or ammonia.

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THE ACTIVITY COEFFICIENT OF EGG ALBUMIN IN THE PRESENCE OF AMMONIUM SULFATE

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The usual method of determining the activity coefficient of a protein in the presence of salt by measuring its solubility is limited, except in the case of globulins, to comparatively concentrated solutions. Furthermore, necessary information concerning the composition of the solid phase is usually lacking, so that one may actually be dealing with a hydrate whose activity is equal to the product of the activity of the protein by some power of the water activity. It may be pointed out that in the inorganic field solutes are usually treated without regard to hydration even though the solid phase, should it exist, contain water of crystallization. One does not, for example, speak of the activity coefficient of hexahydrated calcium chloride.

PROTEIN ACTIVITIES FROM OSMOTIC EQUILIBRIA

The osmotic pressure of protein, both in the presence and in the absence of other substances, has been recently investigated by a number of workers (1, 2, 3). In the following a method will be developed for determining from such measurements what changes are brought about in the activity coefficient of the unhydrated protein by addition of a third component to the solution. The method is applicable at any temperature between the freezing point of water and that temperature at which the protein coagulates, and may be used throughout the entire solubility range of protein and added crystalloid,—organic or inorganic.

Consider an isoelectric protein solution in equilibrium against water across a membrane impermeable to protein but permeable to all other substances. If successive small amounts of salt or urea be added to the system, there will be reached after each addition a new state of equilibrium. By exerting an appropriate pressure the protein molality may be held constant, leaving as the measured variables the osmotic pressure and the molality of added substance within and outside of the membrane.

Suppose the excess pressure above atmospheric on the protein solution reduced from P to zero. Within the membrane when P is reduced to zero, let us set:

a_1 = activity of water.
a_2 = activity of added substance.
a_3 = activity of protein.
m_2 = molality of added substance.
m_3 = molality of protein.
γ_3 = activity coefficient of protein.
$\overline{V}_1$ = partial molal volume of water.
$\overline{V}_2$ = partial molal volume of added substance.

Let $a_1^\#$, $a_2^\#$, $m_2^\#$ represent the corresponding quantities in the protein-free outer solution. The symbols and general method of treatment are those of Lewis and Randall (4). We have the two Duhem equations

$$m_3 \, \mathrm{d} \ln a_3 = -55.51 \, \mathrm{d} \ln a_1 - m_2 \, \mathrm{d} \ln a_2 \tag{1}$$

$$55.51 \, \mathrm{d} \ln a_1^\# = -m_2^\# \, \mathrm{d} \ln a_2^\# \tag{2}$$

Also

$$RT \ln a_1 = RT \ln a_1^\# - \overline{V}_1 P \tag{3}$$

or

$$\mathrm{d} \ln a_1 = \mathrm{d} \ln a_1^\# - \frac{\overline{V}_1}{RT} \mathrm{d}P \tag{4}$$

Similarly

$$\mathrm{d} \ln a_2 = \mathrm{d} \ln a_2^\# - \frac{\overline{V}_2}{RT} \mathrm{d}P \tag{5}$$

Substituting equations 4 and 5 in equation 1,

$$m_3 \, \mathrm{d} \ln a_3 = \frac{55.51\overline{V}_1 + m_2\overline{V}_2}{RT} \mathrm{d}P - 55.51 \, \mathrm{d} \ln a_1^\# - m_2 \mathrm{d} \ln a_2^\# \tag{6}$$

From equations 6 and 2

$$\mathrm{d} \ln a_3 = \frac{55.51\overline{V}_1 + m_2\overline{V}_2}{m_3RT} \mathrm{d}P + \frac{m_2^\# - m_2}{m_3} \mathrm{d} \ln a_2^\# \tag{7}$$

Changing to common logarithms and introducing γ_3

$$\mathrm{d} \log \gamma_3 + \mathrm{d} \log m_3 = \frac{55.51\overline{V}_1 + m_2\overline{V}_2}{2.3 \, m_3RT} \mathrm{d}P + \frac{m_2^\# - m_2}{m_3} \mathrm{d} \log a_2^\# \tag{8}$$

Integrating

$$\int \mathrm{d} \log \gamma_3 = \int \frac{55.51\overline{V}_1 + m_2\overline{V}_2}{2.3 \, m_3RT} \mathrm{d}P + \int \frac{m_2^\# - m_2}{m_3} \mathrm{d} \log a_2^\# - \int \mathrm{d} \log m_3 \tag{9}$$

This equation enables us to calculate changes in γ_3 from measurements of osmotic pressure and the distribution of added substance between the protein-containing and protein-free compartments of an osmometer. The partial molal volumes may be measured or assumed to be the same as in the protein-free solution. Activities outside are determined by the usual methods.

This calculation has been carried through using the careful data of Sörensen (5) and his coworkers on the osmotic pressure of egg albumin in the presence of ammonium sulfate. Since the activity coefficient of ammonium sulfate is not known, it has been assumed equal to that of sodium sulfate as given by Åkerlöf (6). In the calculation of m_3 the molecular weight was taken as 34,500 and the nitrogen factor as 6.45. The value of 55.51 $\overline{V}_1 + m_2\overline{V}_2$ is from table 32, p. 158 of reference 5. In the most dilute salt solution γ_3 is set equal to one.

Table 1 of this paper gives values of m_2^s, m_2, m_3, $\frac{m_2^s - m_2}{m_3}$, $-\log \gamma_2^s$, and $\log a_2^s$ obtained from tables 55, 56, and 57, pp. 334, 335, 336, and 337 of reference 5, and values of γ_2 from reference 6. These are plotted in figure 1 with $\frac{m_2^s - m_2}{m_3}$ as ordinate and $\log a_2^s$ as abscissa. A smooth curve through these points permits a graphical integration of the second term of the right-hand member of equation 9. The first term of the same member contributes little to $\log \gamma_3$ and is easy to evaluate. The quantity

$$\frac{55.51\overline{V}_1 + m_2\overline{V}_2}{2.3\ m_3RT}$$

is found to be approximately constant, so that one may use an average value over any interval and set

$$\frac{1}{2.3RT}\int_{P_1}^{P_2}\frac{55.51\overline{V}_1 + m_2\overline{V}_2}{m_3}\,dP = \frac{1}{2.3RT}\int_{P_1}^{P_2}\frac{\overline{V}}{m_3}\,dP = 5.3 \times 10^{-3}\,(P_2 - P_1) \quad (10)$$

where P is expressed in centimeters of water and $T = 291$.

In table 2 are given the steps in a graphical integration of equation 9. The solutions are selected from table 55, pp. 334 and 335 of reference 5 in such a manner as to cover the concentration range of ammonium sulfate in approximately equal steps. Values for $\frac{m_2^s - m_2}{m_3}$ are read from figure 1. It may be observed that the osmotic pressure term is negligible. Figure 2 shows that the logarithm of the activity coefficient of egg albumin is a linear function of the ammonium sulfate molality within the membrane. The decrease in the activity coefficient of egg albumin with increasing salt

TABLE 1

EXPERIMENT NO.	$m_1^{\#}$	m_1	$m_3 \times 10^3$	$\frac{m_1^{\#} - m_1}{m_3}$	$-\log \gamma_{\pm}^{\#}$	$-\log a_1^{\#}$
98	1.836	1.763	3.657	19.96	0.803	1.015
104	1.761	1.693	3.700	18.38	0.794	1.042
62	1.502	1.433	4.074	16.94	0.761	1.150
112	1.407	1.358	3.374	14.52	0.748	1.198
97	1.388	1.335	3.615	14.66	0.745	1.207
103	1.229	1.186	3.550	12.11	0.722	1.294
61	1.207	1.160	3.932	11.95	0.719	1.309
90	1.183	1.137	3.951	11.64	0.715	1.324
87	1.182	1.140	3.850	10.91	0.714	1.321
89	1.181	1.137	3.921	11.22	0.714	1.324
88	1.178	1.131	3.977	11.82	0.714	1.327
163	1.170	1.123	4.038	11.64	0.713	1.333
164	1.168	1.123	3.977	11.32	0.712	1.333
137	1.167	1.118	3.580	13.69	0.712	1.333
110	1.046	1.010	3.338	10.78	0.692	1.417
111	1.042	1.004	3.295	11.53	0.691	1.417
105	0.8470	0.8214	3.375	7.59	0.657	1.585
96	0.6537	0.6362	3.461	5.06	0.619	1.810
146	0.3283	0.3200	3.193	2.60	0.521	2.410
95	0.3191	0.3133	3.336	1.74	0.517	2.437
94	0.1945	0.1930	3.381	0.44	0.446	2.869
93	0.1299	0.1305	3.349	−0.18	0.396	3.244
82	0.0677	0.0686	3.772	−0.24	0.320	3.865
92	0 0642	0.0633	3.186	+0.28	0.315	3.877
81	0.0336	0.0349	3.772	−0.34	0.250	4.570
91	0.0331	0.0347	3.350	−0.48	0.246	4.576
117	1.577	1.518	3.445	17.12	0.772	1.120
114	1.519	1.463	3.396	16.49	0.764	1.144
108	1.412	1.355	3.500	16.29	0.749	1.195
116	1.209	1.161	3.315	14.48	0.719	1.309
113	1.030	0.9960	3.274	10.38	0.690	1.429
115	0.8209	0.7979	3.282	7.01	0.652	1.612
107	0.6812	0.6605	3.194	6.48	0.624	1.771
129	0.3291	0.3216	3.145	2.39	0.522	2.413
122	0.1923	0.1907	3.233	0.50	0.445	2.881
121	0.1298	0.1279	3.140	0.61	0.396	3.247
84	0.0680	0.0679	3.851	0.03	0.322	3.868
120	0.0637	0.0635	3.086	0.06	0.315	3.931
83	0.0331	0.0332	3.802	−0.03	0.246	4.576
119	0.0317	0.0318	3.087	−0.03	0.242	4.621
167	1.531	1.478	3.452	15.35	0.766	1.141
166	1.407	1.352	3.587	15.33	0.748	1.198
127	1.193	1.154	3.333	11.70	0.716	1.315
165	1.081	1.046	3.515	9.96	0.698	1.390
106	1.039	1.009	3.435	8.73	0.691	1.420
168	0.7625	0.7591	3.693	9.20	0.641	1.675
133	0.3312	0.3249	3.092	2.04	0.523	2.407

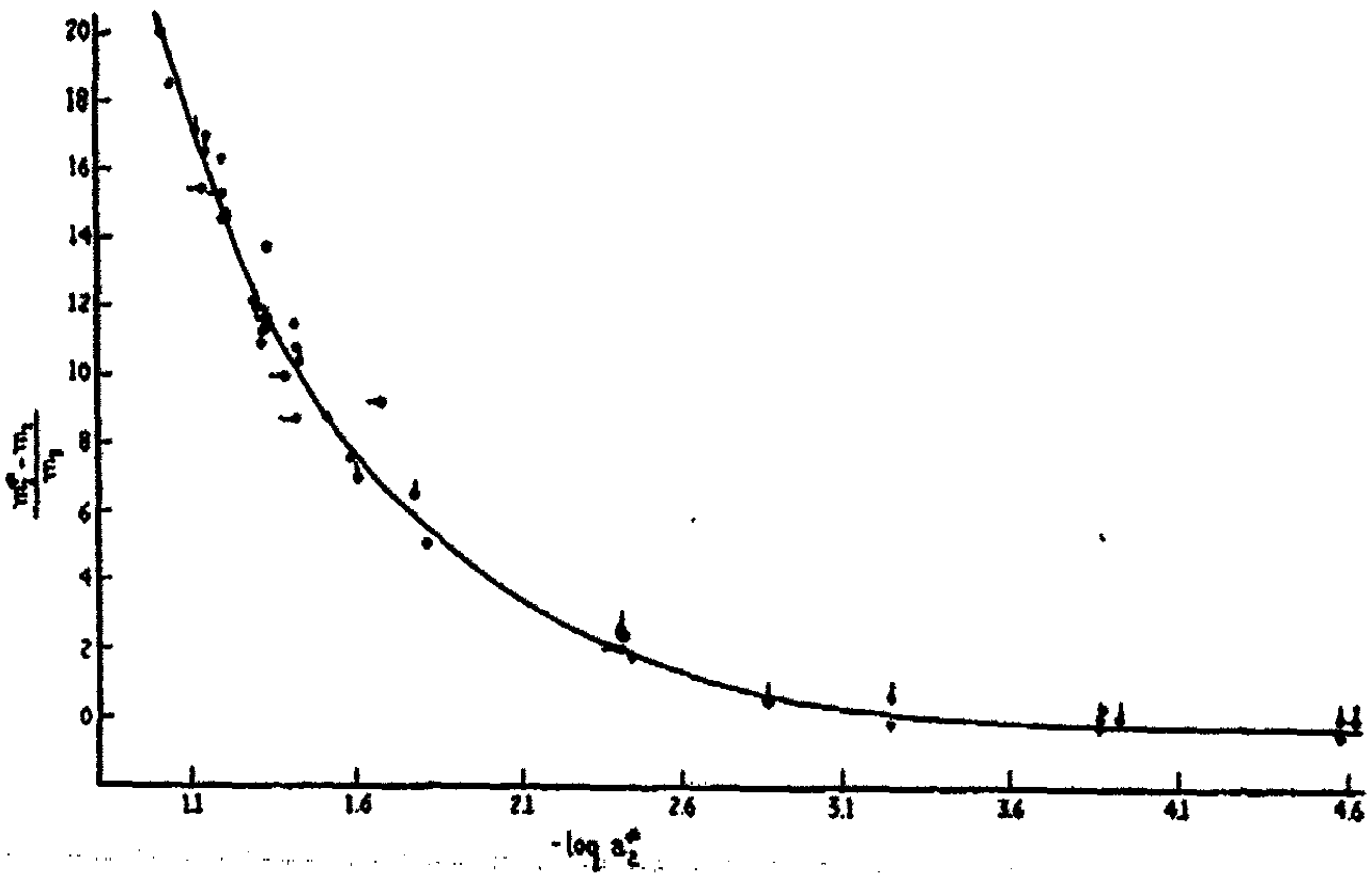

FIG. 1.

| Solutions of pH 4.6; • solutions of pH 4.9; → solutions of pH 5.3

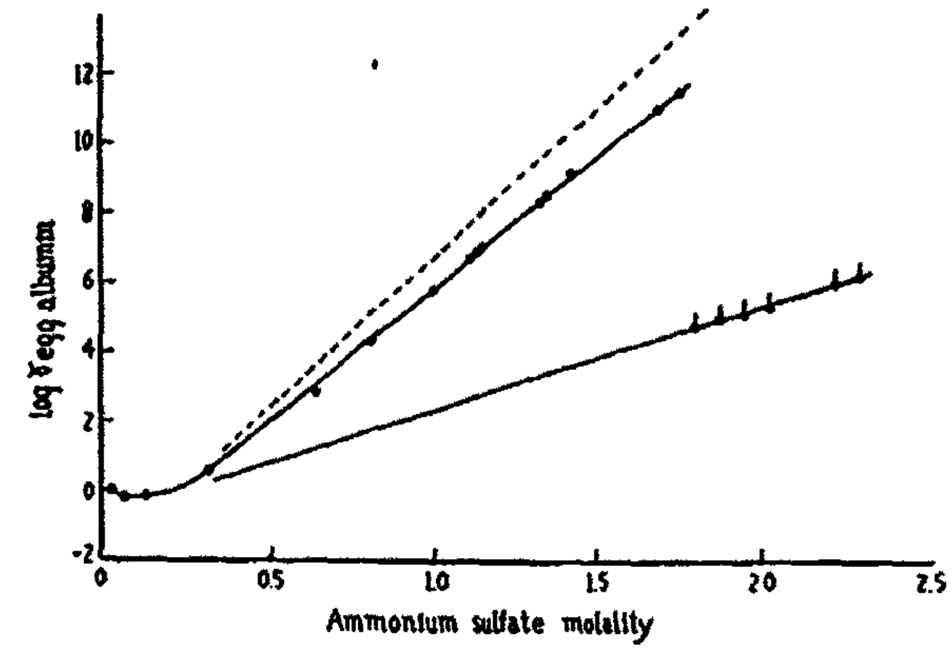

FIG. 2.

• Log activity coefficient egg albumin from osmotic equilibria.

| Log activity coefficient egg albumin from solubilities, assuming $\log \gamma$ = Constant − $\log m_3$.

The broken line shows log activity coefficient egg albumin from solubilities corrected for changing water activity, assuming the solid phase to contain 0.22 g. water per gram of protein. In the case of the two curves from solubilities only the slopes are significant.

concentration at low salt concentrations may be real, as in the case of globulins, or may possibly be an error due to a small amount of ammonia in the egg albumin, which would reverse the sign of $\frac{m_2^* - m_2}{m_3}$. The author is inclined to accept the first interpretation.

TABLE 2

EXPERIMENT NO.	m_2	$m_3 \times 10^3$	V	P	$\frac{1}{2.3\,RT}\int\frac{V}{m_3}\,d\,P$	$\frac{m_2^* - m_2}{m_3}$	$-\log a_2^*$	$\int\frac{m_2^* - m_2}{m_3}\,d\log a_2^*$	$-\int d\log m_3$	$\log\gamma_3$
91	0.03	3.35	1003	73.1	0	−0.3	4.576	0	0	0
82	0.07	3.77	1005	79.5	+0.03	−0.2	3.865	−0.18	0.06	−0.21
93	0.13	3.35	1008	75.7	+0.01	+0.1	3.244	−0.18	0	−0.17
95	0.31	3.37	1019	73.7	0	1.8	2.437	+0.59	0.01	+0.58
96	0.64	3.46	1039	73.1	0	5.5	1.810	2.88	0.02	2.86
105	0.82	3.38	1052	67.9	−0.03	7.9	1.585	4.38	0.01	4.34
111	1.00	3.30	1064	62.1	−0.06	10.3	1.417	5.91	0	5.85
137	1.12	3.58	1072	61.7	−0.07	11.7	1.333	6.84	0.03	6.74
90	1.14	3.95	1073	72.3	0	12.0	1.324	6.94	0.08	6.86
61	1.16	3.93	1075	66.8	−0.03	12.2	1.309	7.13	0.07	7.03
97	1.34	3.62	1087	58.2	−0.07	14.6	1.207	8.49	0.03	8.39
112	1.36	3.37	1088	53.0	−0.10	14.8	1.198	8.62	0.01	8.51
62	1.43	4.07	1095	59.3	−0.07	16.0	1.150	9.36	0.09	9.20
104	1.69	3.70	1112	43.9	−0.15	19.2	1.042	11.26	0.05	11.06
98	1.76	3.66	1118	39.6	−0.17	20.0	1.015	11.79	0.04	11.58

TABLE 3

EXPERIMENT NO.	m_2	$m_3 \times 10^5$	$\log m_3 + 5$	$1.57 - \log m_3$
1	1.81	59.42	1.77	4.80
2	1.88	40.17	1.60	4.97
3	1.95	26.18	1.42	5.15
4	2.03	14.98	1.18	5.39
5	2.22	3.467	0.54	6.03
6	2.29	2.080	0.32	6.25

PROTEIN ACTIVITIES FROM MEASUREMENTS OF SOLUBILITY

That the solubilities of proteins are affected by salts has long been known. Cohn (7) pointed out that the logarithm of protein solubility is, in the case of egg albumin and of pseudoglobulin, a linear function of salt concentration. This relation has since been found by Florkin (8) to hold for fibrinogen, and by Green (9) for hemoglobin. It is sometimes assumed that

$$\log \gamma_{\text{protein}} = \text{Constant} - \log \text{Solubility}_{\text{protein}} \qquad (11)$$

and a calculation made in accordance with the above from table 39, p. 221 of reference 5 is shown in table 3 and plotted in figure 2.

One may see that a great discrepancy exists between the slope of the straight line through these points and the values of log γ_3 obtained by the previous method. If the solid phase contains water as water of crystallization and we choose unhydrated protein as one component, however, equation 11 cannot hold. The reaction is not

$$\text{Protein (dissolved)} \rightleftharpoons \text{Protein (solid)} \qquad (12)$$

but

$$\text{Protein (dissolved)} + n\text{H}_2\text{O} \rightleftharpoons \text{Protein hydrate (solid)} \qquad (13)$$

so that if a_1 = activity of water,
m_2 = molality of ammonium sulfate,
a_3 = activity of protein,
m_3 = solubility of protein,
γ_3 = activity coefficient of protein,
a_4 = activity of protein hydrate, and
n = moles of water per mole of protein in the hydrate,

$$a_1^n \cdot a_3 = a_4 = \text{Constant} \qquad (14)$$

therefore

$$n \, d \log a_1 + d \log \gamma_3 + d \log m_3 = 0 \qquad (15)$$

and

$$\frac{\partial \log \gamma_3}{\partial m_2} = -\frac{\partial \log m_3}{\partial m_2} - n \frac{\partial \log a_1}{\partial m_2} \qquad (16)$$

but

$$\frac{\partial \log a_1}{\partial m_2} = \frac{\partial \log a_1}{\partial \theta} \frac{\partial \theta}{\partial m_2} \qquad (17)$$

where θ is the freezing point depression.

$$\frac{\partial \log a_1}{\partial \theta} = -0.00421 \qquad (18)$$

(See reference 4, p. 284.) Also for ammonium sulfate (reference 10), when m_2 is about 2,

$$\frac{\theta}{m_2} = 3.21 \qquad (19)$$

We shall set $\frac{\partial \theta}{\partial m_2}$ equal to this, and neglect the effect of protein on a_1. Solid egg albumin hydrate contains 0.22 g. of water per gram of protein (reference 5, p. 210).

$$n = \frac{34{,}500 \times 0.22}{18} = 422 \tag{20}$$

From table 3

$$-\frac{\partial \log m_3}{\partial m_2} = 3.0 \tag{21}$$

Thus

$$\frac{\partial \log \gamma_3}{\partial m_2} = 3.0 + 422 \times 0.00421 \times 3.21 = 8.7 \tag{22}$$

which agrees satisfactorily with the slope 7.6 obtainable from table 2 when one considers all the assumptions made in getting constants necessary for the computation, and the fact that in one case the protein concentration is held constant while in the other it varies greatly.

SUMMARY

The logarithm of the activity coefficient of egg albumin in the presence of ammonium sulfate has been calculated from osmotic data and found to be a linear function of the salt concentration. These activity coefficients are in satisfactory agreement with solubility measurements when account is taken of the composition of the solid phase.

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NEW BOOKS

Réel et Déterminisme dans la Physique Quantique. By E. Meyerson, with a preface by L. de Broglie. 50 pp. Monograph No. 68 of the scientific and industrial series published by Hermann & Co., Paris, 1933.

This volume is the first of a group of monographs published under the direction of Professor L. de Broglie on the philosophy of the sciences. These philosophical treatises are to be part of the large scientific series mentioned. In the present essay the concepts of physical science are discussed in the light of quantum theory. References are given to the author's own works and to seven original articles. No headings, no subdivisions, no index, and the discursive style make the volume very slow reading when one considers the difficult subject matter dealt with.

George Glockler.

Wege zur physikalischen Erkenntnis. Reden und Vorträge. By Max Planck. 22.5 x 15 cm.; ix + 280 pp. Leipzig: S. Hirzel, 1933. Price: bound, 8 marks; unbound, 6 marks.

Professor Planck has collected in this volume eleven lectures, given over a period from 1908 to 1933, in which the central theme is the physical conception of the universe and its reactions on philosophy. The physicist's picture of the universe has changed during this period very considerably, and in recent times it has seemed to some that all hope of retaining the law of causality, and of going beyond the purely formal descriptions of events by mathematical methods, would have to be abandoned. Professor Planck, whose own work has been most concerned in this change of outlook in physics, does not adopt this rather pessimistic view, and in this series of lectures he has examined the consequences of each new step in the physical description of events. The lectures are, in fact, the result of careful thought on the part of a scientist who has always tried to see beyond the narrow walls of the physical laboratory, and the volume is one in which former students of the great physicist will recognize his inimitable command of his subject and the great power of exposition and logical clarity which characterize all his work. The Nobel Lecture on the quantum theory is included. The volume is one of considerable interest and value.

J. R. Partington.

The Cotton Effect. By S. Mitchell. 22 x 13.5 cm.; vii + 92 pp. London: G. Bell and Sons, 1933. Price: 7 s. 6 d.

The opening chapter of this excellent little book is devoted to a consideration of the fundamental conceptions of refractive dispersion, normal and anomalous dispersion, double refraction, plane, circular, and elliptical polarization, circular double refraction, anomalous rotatory dispersion, the detection of elliptical vibration, the Cotton effect, and circular dichroism. These terms and the causes of the various phenomena are fully explained, together with an account of the history of the work which led to their recognition. This is followed by a description of the measurement of absorption spectra. The Hartley method and its modifications are described, as also are the uses of the spectrophotometer and the polarization-photometer. The third chapter is devoted to theoretical considerations and in this the equations of Sellmeier and Drude, connecting refractive dispersion and absorption, are considered together with the modern developments of Kuhn. The measurement of rotation and ellipticity with modern instruments constitutes the subject of the fourth chapter. The work of Tschugaev, Lowry and others on rotatory dispersion and circular dichroism in connection with a number of organic and inorganic substances is dealt with in the next chapter, whilst the final chapter deals with asymmetrical photochemical action. Here many unsuccessful attempts at asymmetric synthesis are described, together with the technique of the author which led to successful results.

The book presents an excellent summary of the present knowledge of the subject and it can be recommended with confidence.

JAMES F. SPENCER.

The Conductivity of Solutions. By C. W. DAVIES. 2nd edition. 21.5 x 14 cm.; x + 281 pp. London: Chapman and Hall, 1933. Price: 15s.

Since the first edition of this book was reviewed in The Journal of Physical Chemistry in 1930, it is only necessary to say that the size has been increased by about eighty pages by the inclusion of new material, two extra chapters on the practical applications of conductivity measurements having been added, and several of the sections in the earlier text have been brought up to date by the inclusion of recent work. A brief account of Wien's experimental method and the results, further investigations on non-aqueous solutions, the dissociation of weak ternary electrolytes, the recent investigations on the viscosity of electrolytes, and a very brief mention of the theory of Gronwall, La Mer, and Sandved are the principal additions. The accounts of the theories are very sketchy and the mathematical side of the subject is neglected. On the other hand, the numerical applications of the equations, which are assumed, are good, and there are useful tables of data.

J. R. PARTINGTON.

Theoretical Physics. Vol. I. Mechanics and Heat (Newton-Carnot). By W. WILSON. 325 pp.; 80 diagrams. New York: E. P. Dutton & Co., 1932.

The author covers the usual field of mathematical physics. Chapters I and II cover an introduction to vector and tensor analysis, the theorem of Gauss, Green and Stokes and Fourier's expansion. Dynamics, wave propagation, elasticity, hydrodynamics, and viscous fluids are dealt with in chapters III to IX. The kinetic theory of gases and statistical mechanics take up chapters X and XI and the first and second laws of thermodynamics with applications conclude the volume in chapters XII to XIV. The book is written in mathematical language, of course, and the explanatory paragraphs written in ordinary language are short, concise, and reduced to the minimum. Because he uses the concise expressions of mathematics, the author can cover the tremendous fields of human thought outlined above and do it well in the allotted space. The student who wishes to read further about the subject matter will welcome the bibliography added at the end of each chapter. This volume is the first one of three on the subject of theoretical physics; the second and third volumes are to cover electromagnetism, optics and relativity, quantum dynamics respectively. The first volume is an excellent treatise on the topics covered and the other volumes of the set will be awaited with great interest.

GEORGE GLOCKLER.

Lehrbuch der physikalischen Chemie. By KARL JELLINCK. Band IV, Lieferung 3. 25 x 16.5 cm.; xiv + 625-890 pp. Stuttgart: F. Enke, 1933. Price: 26 marks.

The present issue completes the fourth volume of the work, and a fifth volume is to appear. The subject dealt with is the phase rule, and the treatment is intended to be representative rather than exhaustive. One- and two-component systems are treated by means of representative examples, a good feature being the inclusion of uncondensed systems in some detail, since this subject, being perhaps rather more difficult, tends to be neglected. Quantitative work is introduced when available, and the diagrams are plentiful and well drawn. In the treatment of three-component systems with one liquid and one or more solid phases, the Schreinemaker isothermal method is generally used, but a few examples of the van't Hoff method are also given. There is a section on thermal analysis as applied to three-component systems, and the usual detailed discussion of double salts with and without transition points. Mixed crystallization in three-component systems, and uncondensed ternary systems are dealt with only briefly, but references to literature are given fully throughout. Four-component systems are represented by reciprocal salt pairs, and by a system composed of water and three salts with a common ion. No higher systems are treated. The book provides a compact and clear account of a large subject, and maintains the high standard of previous volumes. It is a work of great merit and should be available to all physical chemists.

J. R. PARTINGTON.

Essai sur la Chimie Comparée. Les Corps Simples. By IONEL N. LONGINESCU. 25 x 16 cm.; vii + 98 pp. Paris: Les Presses Universitaires de France, 1932. Price: 30 francs.

The opinion of the author of this essay is that the comparative method is the one best suited both to the progress of and to the learning of a science. As in the case of comparative anatomy the animal may be constructed by the aid of a single organ, so from knowledge of a single property of a substance, all others might be derived, or the relations traced from family to family.

An electrochemical, thermochemical, photochemical, and analytical classification of the chemical elements is considered, but the basis actually adopted is a modification of the Mendeléeff periodic system. There is thus very little that is novel in the presentation, with a tendency rather to emphasize similarity and to ignore differences.

The author states that he may, at a later date, deal with binary substances; if he does, it will be interesting to see how these will fare under the comparative method.

W. H. PATTERSON.

Fortschritte der Serologie. By HANS SCHMIDT. Vol. XXX of "Wissenschaftliche Forschungberichte." 22 x 15 cm.; xi + 191 pp. Dresden and Leipzig: Theodor Steinkopff, 1933. Price: bound, 13.20 RM; unbound, 12.00 RM.

The series of "Wissenschaftliche Forschungsberichte," of which the present work is a number, undertakes to sift the chaff from the wheat and so differs from the somewhat distressing compilations with which we are familiar in German literature. The present volume consists of a survey of the present state of serology, using this term in the strict sense as applying to phenomena observed in the test tube. All reference to immunity and anaphylaxis is excluded, these being dealt with in another volume. It is not to be supposed that a specialist in serological reactions will find this review of much use to him, but the worker in allied subjects will welcome it as a survey of a field which is possibly overloaded with minutiae. The author, in order to produce anything but a trivial account in less than two hundred pages, has naturally been forced to pick and choose. Some subjects are frankly referred to recent reviews after a mere introductory outline, but those which are of considerable topical interest, such as the chemical nature of antigens and their bearing upon agglutination, are dealt with critically and fully from the point of view of presenting a broad outline, though not of course in the matter of detail. For those who may require it, two sources of further information are provided, namely, references to the authors cited, which indicate a special regard for the work of British and American workers, and references to more extensive reviews in different languages.

P. Fildes.

James Clerk Maxwell. 146 pp. New York: The Macmillan Co. Price: $2.50.

This is a commemoration volume containing essays by J. J. Thomson, Planck, Einstein, Larmor, Jeans, Garnett, Fleming, Lodge, Glazebrook, and Lamb.

It is apparent that those who through direct personal acquaintance or who through closely allied intellectual achievement could speak authoritatively were called upon to participate directly in the centenary of Maxwell's birth and it is inevitable that those whose intellectual interests lie in the fields of physics, chemistry, and mathematics will greatly appreciate the evaluations given in these essays. The laity however will appreciate the volume only in part because of the profoundly technical character of Maxwell's work.

The volume has an additional interest in that it gives the reader the reactions of master minds at a time when new concepts are in the foreground.

Henry A. Erikson.

Gmelin's Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System Number 35: Aluminium. Teil B, Lieferung 1: Die Verbindungen des Aluminiums. 25.5 x 17.5 cm.; ix + 308 pp. Berlin: Verlag Chemie, 1933. Price: 48 marks. Subscription price: 42 marks.

The present volume deals with the oxides, oxide hydrates, nitride, halogenides, sulfate, and several less important compounds. The technical processes are fully dealt with, including aluminum chloride for oil cracking, and recent literature and patents are very fully covered. The recent papers of Weiser and Milligan, and of Edwards and Tosterud, in This Journal came too late for inclusion in the literature on the oxide hydrates, but the book by Edwards, Frary, and Jeffries on the aluminum industry is frequently cited and the technical information is complete and up-to-date. The volume is an indispensable addition to the literature of chemistry.

J. R. Partington.

L'Univers en Expansion. By Henri Mineur. Actualités Scientifiques et Industrielles, No. 63. Publiés sous la direction de M. L. de Broglie. Paris: Hermann & Cie, 1933.

The present volume is No. 63 in the series of monographs on scientific subjects, chiefly those in theoretical physics, published under the direction of de Broglie. It gives one of the very few up-to-date discussions of the subject, which is not merely intended for the layman or the general public, but treats the entire problem concisely, "from the ground up," using directly the equations of Einstein, de Sitter, Lemaître, and others, and discusses the properties of the various types of space resulting from each. It closes with a résumé of Eddington's calculations of the cosmological constant λ. It is clearly written, and gives an admirable summary of this *question brulante* of the present, and may be heartily recommended to any one interested in the problem.

W. J. Luyten.

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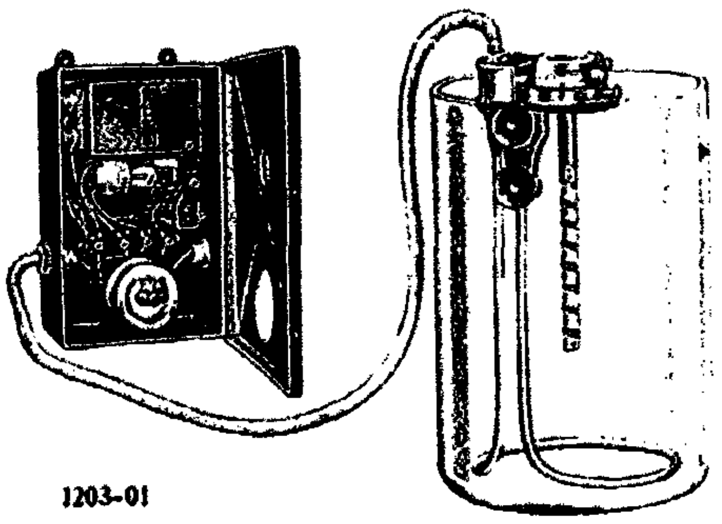

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THE SOLUBILITY OF ACETYL-O-TOLUIDINE IN VARIOUS SOLVENTS[1]

J. L. HALL,[2] A. R. COLLETT, AND C. L. LAZZELL

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Received July 8, 1933

INTRODUCTION

In previous communications to This Journal, Collett and Lazzell have reported a series of measurements of solubility for several systems of disubstituted benzene derivatives, namely the nitroanilines (1), the aminobenzoic acids (2), the nitrobenzoic acids (3), and the dihydroxybenzenes (4).

A survey of the literature revealed that no systematic investigation of the solubility of the acetyltoluidines in a series of solvents had ever been reported. The present investigation was undertaken with the primary object of obtaining data for another system of disubstituted benzene derivatives which could be used in the study of the solubility relations of systems of this type. These measurements are of value in themselves, since the acetyltoluidines are of some commercial importance.

In this paper are presented solubility measurements for acetyl-*o*-toluidine in methyl alcohol, ethyl alcohol, *n*-propyl alcohol, isopropyl alcohol, *n*-butyl alcohol, isobutyl alcohol, acetone, chloroform, carbon tetrachloride, benzene, diethyl ether, and water from about 25°C. to 110.3°C., the melting point of the solute. The heat of fusion of acetyl-*o*-toluidine has been calculated.

MATERIALS

A. *Acetyl-o-toluidine*

The acetyl-*o*-toluidine used in these determinations was the best grade obtainable from the Eastman Kodak Company. As received, it had a melting point of 107.1°C. After one crystallization from water it melted at 110.3°C. A little tar was observed to be formed around the beaker. A second crystallization from water gave no tar and no further change in

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[1] Contribution No. 92 from the Department of Chemistry, Division of Industrial Sciences of West Virginia University.

[2] From a part of the thesis presented to the Graduate School of West Virginia University, in June 1932, by James Lester Hall in candidacy for the degree of Master of Science.

melting point. Recrystallization of this product from alcohol gave no further change in melting point. For this reason it was concluded that the material which had been crystallized from water once and thoroughly dried was of sufficient purity for use. The melting point given in the International Critical Tables is 110.3°C. Before using, the material was dried over calcium chloride and then over concentrated sulfuric acid.

B. Solvents

All the solvents used in this investigation, except water, were carefully dried and distilled several times until a product having a satisfactory boiling range was obtained. Freshly redistilled water was used. In table 1 are listed the boiling ranges and the refractive indices of the solvents used. All temperatures were obtained by use of thermometers certified by the Bureau of Standards and corrections were made in each case for stem emergence. The boiling ranges were all reduced to 760 mm. pressure.

TABLE 1

Physical properties of solvents

SOLVENT	BOILING RANGE	BOILING POINT (INTERNATIONAL CRITICAL TABLES)	REFRACTIVE INDEX	
			Found	International Critical Tables
	degrees C.	*degrees C.*		
Methyl alcohol	64.3	64.5	1.3291	1.329
Ethyl alcohol	78.4	78.5	1.3618	1.361
n-Propyl alcohol	97.1	97.8	1.3854	1.386
Isopropyl alcohol	82.0–82.2	82.3	1.3790	1.378
n-Butyl alcohol	117.9	117.7	1.3992	1.3993
Isobutyl alcohol	106.9–107.0	107.3	1.3958	1.396
Benzene	79.98–80.02*	79.6	1.5012	1.5014
Acetone	55.8–56.0	56.1	1.3599	1.3591
Carbon tetrachloride	76.5	76.8	1.4603	1.4607
Chloroform	60.8–61.1	61.2	1.4461	1.4467
Diethyl ether	34.25–34.35	34.5	1.3528	1.3526

* Richards and Barry (J. Am. Chem. Soc. 37, 996 (1915)) give 80.2°C. as the boiling point of benzene.

METHOD

The experimental data on solubility presented in this article were obtained by the synthetic method. Details of the procedure used here are fully explained in a previous paper (5).

All of the determinations were checked by at least two trials and many were repeated by duplicate bulbs.

TABLE 2

Experimental values of the solubility of acetyl-o-toluidine in terms of mole percentage

C	*t*	*C*	*t*	*C*	*t*
Methyl alcohol		Ethyl alcohol		*n*-Propyl alcohol	
	degrees C.		*degrees C.*		*degrees C.*
100.00	110.3	100.00	110.3	100.00	110.3
86.00	102.4	85.50	102.0	86.80	103.2
83.60	100.7	79.95	99.2	63.30	87.4
74.35	94.9	71.90	93.5	53.20	79.2
69.50	91.0	64.60	87.7	49.38	76.2
63.60	86.5	54.94	80.8	40.40	68.9
59.80	83.3	47.55	75.2	32.30	60.0
55.48	79.6	41.37	69.9	20.15	45.0
45.55	71.0	31.80	60.3	15.18	36.7
36.45	61.4	24.45	52.3		
26.50	47.9	13.99	34.8		
22.34	42.1	9.20	23.9		
10.31	18.3				
Isopropyl alcohol		*n*-Butyl alcohol		Isobutyl alcohol	
100.00	110.3	100.00	110.3	100.00	110.3
92.80	106.2	88.20	103.5	87.60	103.1
82.20	100.2	67.80	90.6	78.80	98.0
72.50	94.4	63.10	86.7	67.92	91.4
61.10	86.7	50.35	77.2	57.90	83.0
51.70	79.8	42.14	70.8	50.06	77.2
41.30	71.8	33.40	62.1	42.35	72.3
33.94	66.0	21.58	47.7	30.51	60.7
25.61	57.1	10.50	26.5	20.74	49.2
23.13	54.1			10.30	30.1
21.72	52.2				
11.31	34.5				
Benzene		Acetone		Carbon tetrachloride	
100.00	110.3	100.00	110.3	100.00	110.3
87.82	103.6	91.60	105.5	91.24	105.7
80.30	98.6	82.52	100.3	77.75	98.1
69.48	92.6	71.30	93.4	66.73	91.9
60.30	87.2	68.50	91.6	59.63	88.0
44.54	76.8	52.82	79.9	49.44	81.8
35.97	71.5	38.37	68.1	38.06	75.4
27.68	65.8	29.01	58.7	29.92	71.0
18.26	59.3	19.16	46.0	20.57	66.2
9.78	52.3	11.43	31.2	11.35	61.1
7.22	49.6			6.21	57.7
3.00	40.8			2.313	52.2
				.718	41.1

TABLE 2—*Concluded*

C	t	C	t	C	t
Chloroform		Diethyl ether		Water	
	degrees C.		*degrees C.*		*degrees C.*
100.00	110.3	100.00	110.3	100.00	110.3
89.30	104.1	91.90	106.2	Forms a triple point at 79.6°C. over an undetermined range	
79.80	98.0	79.70	99.9		
76.90	96.0	70.03	95.2		
61.70	83.2	60.55	90.4		
52.90	74.1	47.72	84.6		
45.42	64.8	35.90	80.0		
35.65	50.7	24.96	76.0		
28.11	38.2	12.85	70.8		
21.00	22.1	5.900	63.4	0.380	69.0
		2.288	48.7	0.1743	43.3
		1.146	27.7		
		Ideal			
		100.00	110.3		
		90.00	105.0		
		80.00	99.2		
		70.00	92.9		
		60.00	85.8		
		50.00	77.9		
		40.00	68.4		
		30.00	57.2		
		20.00	42.4		
		10.00	20.1		

EXPERIMENTAL RESULTS

The experimental measurements of the solubility of acetyl-*o*-toluidine are listed in table 2, C being the molal percentage of the solute ($C = 100\,N$, where N is the mole fraction of the solute) and t the temperature in degrees Centigrade. The thermometers used were checked against thermometers calibrated by the Bureau of Standards. All readings were corrected for emergent stems.

The results marked "ideal" were calculated as will be explained in the next part of this paper. The results presented in table 2 were plotted on a large scale in terms of C versus t, and from these curves values of solubility have been obtained at 5-degree intervals of temperature. Table 3 was constructed from these values.

TABLE 3

Solubility of acetyl-o-toluidine in various solvents, interpolated at a series of temperatures, expressed in terms of mole percentage

TEMPERATURE	METHYL ALCOHOL	ETHYL ALCOHOL	*n*-PROPYL ALCOHOL	*n*-BUTYL ALCOHOL	ISO-PROPYL ALCOHOL	ISO-BUTYL ALCOHOL	BENZENE	CARBON TETRACHLORIDE	CHLOROFORM	ACETONE	DIETHYL ETHER
25	15.6	9.5	—	10.0	—	8.2	—	—	22.1	8.7	0.9
30	17.7	11.6	12.0	12.0	9.3	10.2	.	.	24.2	10.8	1.3
35	19.8	14.0	14.4	14.4	11.6	12.7	0.8	0.6	26.5	13.2	1.5
40	22.2	16.4	17.0	17.0	14.0	15.0	2.2	0.7	29.1	15.5	1.8
45	24.7	19.3	20.0	20.0	16.8	17.8	4.3	0.8	32.1	18.4	2.0
50	27.9	22.7	23.5	23.3	20.1	21.2	7.5	1.5	35.2	31.9	2.4
55	31.4	26.8	27.6	27.2	23.9	25.2	12.6	3.7	38.5	25.7	3.1
60	35.4	31.5	32.3	31.5	28.5	29.7	19.2	9.5	42.0	30.2	4.5
65	39.7	36.3	37.0	36.0	33.5	34.4	26.8	13.4	45.5	35.1	6.9
70	44.6	41.5	42.3	41.2	39.2	39.8	34.0	28.0	49.5	40.5	11.7
75	50.2	47.4	47.9	47.4	45.5	46.0	41.5	37.3	53.7	46.6	22.0
80	56.0	53.9	54.3	54.0	52.0	52.3	49.4	46.0	58.5	53.0	36.0
85	61.9	60.5	61.0	60.7	58.6	59.0	56.9	54.5	63.5	59.7	47.7
90	68.2	67.0	67.2	67.0	65.8	65.9	65.0	63.2	69.4	66.4	59.7
95	74.7	74.1	74.1	74.7	73.5	73.6	73.3	72.0	75.7	73.8	69.8
100	82.1	81.8	81.6	82.1	81.7	81.8	81.8	81.0	82.9	81.8	79.9
105	90.6	90.5	90.0	90.6	90.3	90.4	90.3	89.8	90.9	90.5	89.6
110.3	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

DISCUSSION OF RESULTS

As far as could be determined, the heat of fusion of acetyl-*o*-toluidine has not been reported. It will be noted by inspection of the solubility curves (figure 1) that they all approach the melting point of the solute at approximately the same slope. Since a solution of the type studied here will be nearest to the ideal at high concentrations of the solute, it is reasonable to suppose that this slope is approximately the slope of the ideal solution curve. The molal heat of fusion was obtained from the slope of curves secured by plotting log N versus $1/T$ and by substitution in the usual ideal solubility equation,

$$\log N = \frac{-L_f}{4.58}\left(\frac{1}{T} - \frac{1}{T_m}\right)$$

where log N is the logarithm to the base 10 of the mole fraction of the solute, T_m is the melting point of the solute, T is the solution temperature of a particular system containing an amount of solute to give a mole fraction N, and L_f is the molal heat of fusion. In this way a large number of values were obtained ranging between 5500 and 5900 calories. The average of all values gives 5700 calories for the molal heat of fusion of acetyl-*o*-toluidine.

Using this value for the molal heat of fusion, the ideal solubility curve for acetyl-*o*-toluidine was calculated by solving for T for each 10 mole per cent from 10 to 100.

Figure 1 is a plot of part of the data of table 2. Since the curves for the alcohols are grouped so close together, only three are shown. The ideal curve is also shown. Figure 2 shows the curves for the alcohols on an enlarged scale over part of their range.

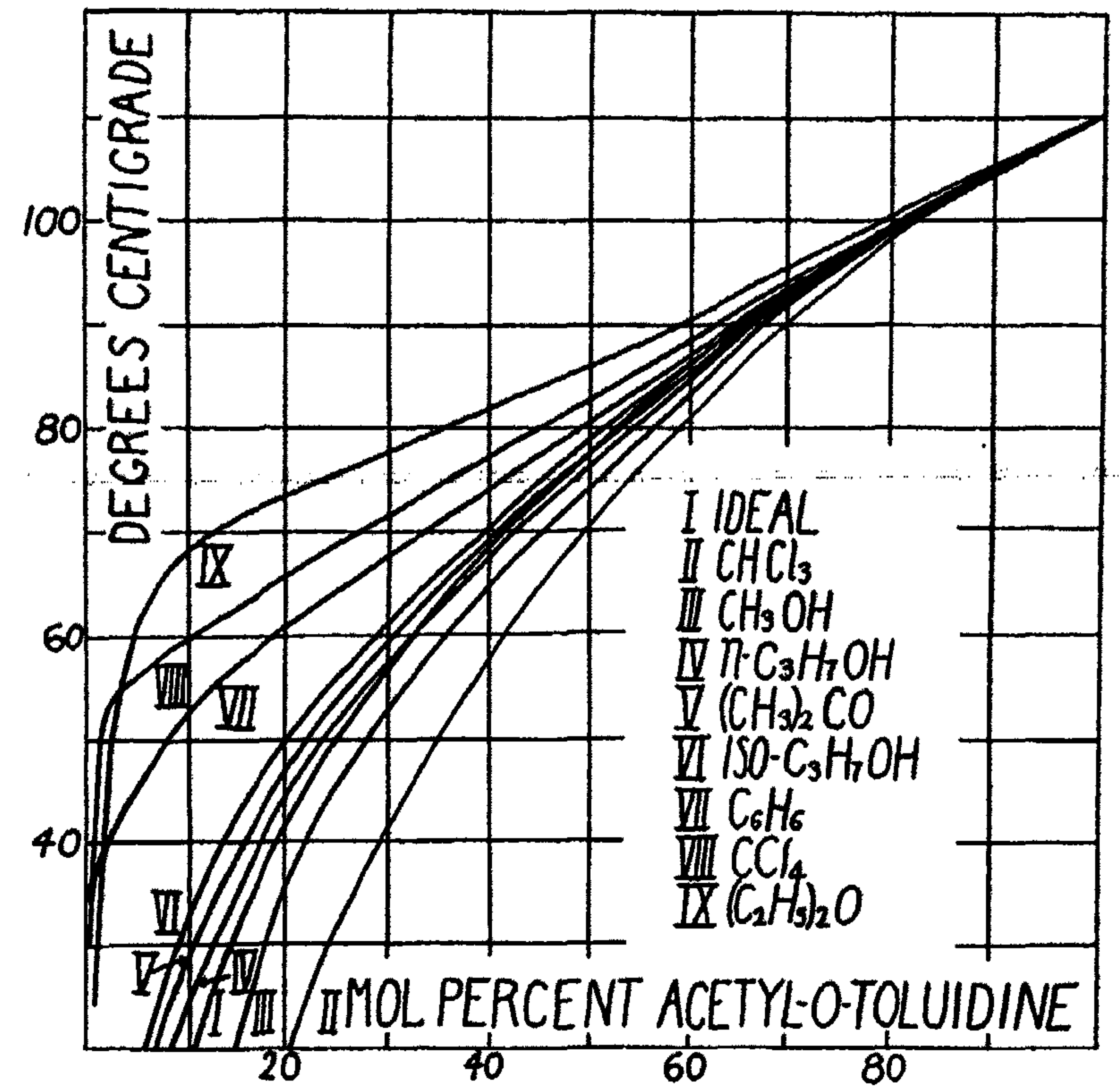

FIG. 1. SOLUBILITY CURVES FOR ACETYL-*o*-TOLUIDINE IN VARIOUS SOLVENTS

Except for methyl alcohol, the solubility curves for the alcohols and acetyl-*o*-toluidine form a very narrow band. This band is approximately coincident with the ideal curve above 60 mole per cent and shows increasing divergence below this point. Arrangement of the alcohols in descending order as to solvent power gives: methyl, propyl, ethyl, isobutyl, isopropyl. It is interesting to note that, of the alcohols studied, except methyl, propyl has the greatest solvent power, and isopropyl the least, while butyl had next to the greatest solvent power, and isobutyl next to the least. Evidently branching the carbon chain of the alcohol has a greater effect on the amount of acetyl-*o*-toluidine which it will dissolve than does the addition of an atom of carbon to the end of the chain. There is no evident relationship between the melting points of the alcohols and the rate at which the curves break or their relative positions on the sheet.

The curve for acetyl-*o*-toluidine and acetone is in the narrow band formed by the alcohol curves, being midway between the ethyl and isobutyl curves. This curve is very near to the ideal curve above 50 mole per cent. The dielectric constant of acetone is about of the same order as that of the alcohols and this may indicate that there is some relationship between the polarity and the solubility.

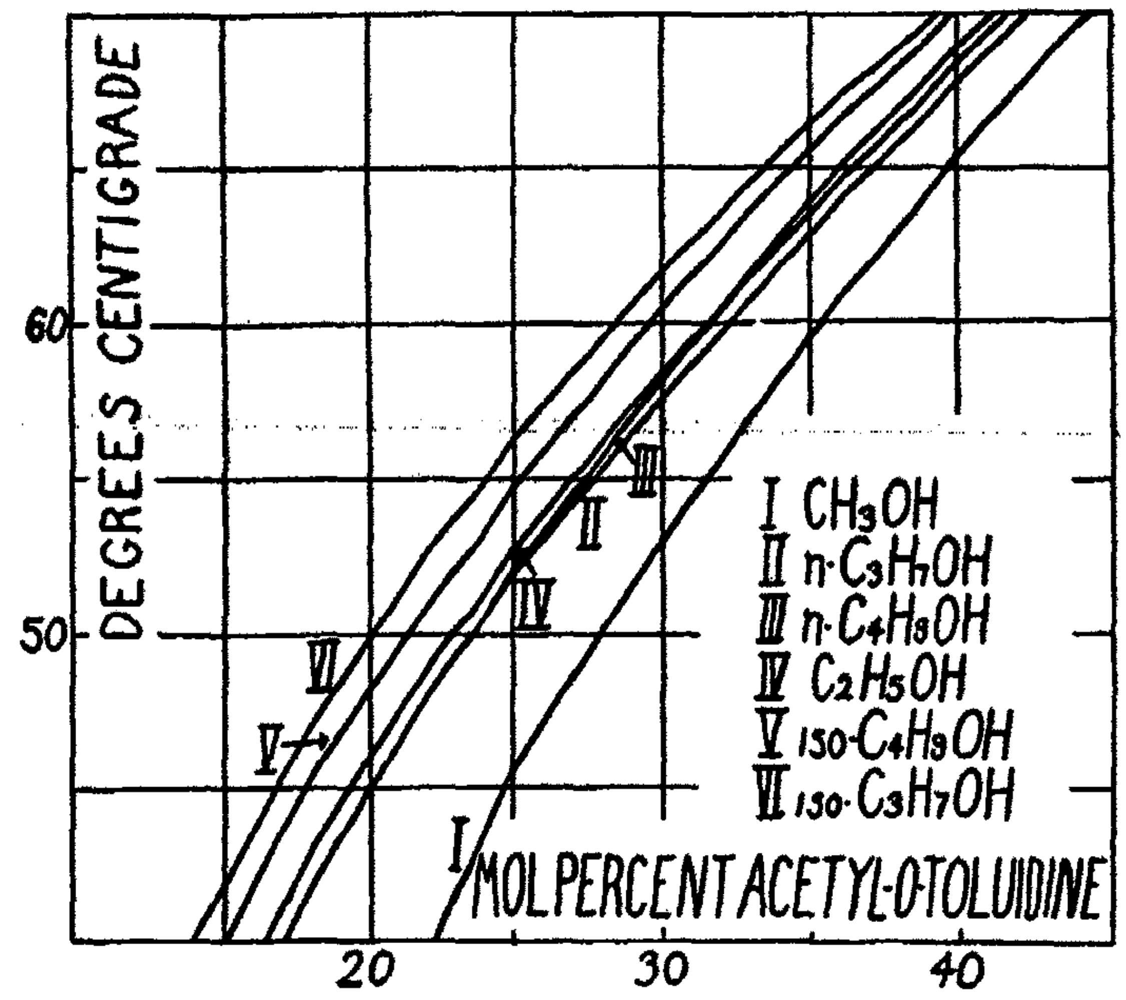

FIG. 2. SOLUBILITY CURVES FOR ACETYL-*o*-TOLUIDINE IN SEVERAL ALCOHOLS

The acetyl-*o*-toluidine was much more soluble in chloroform than in any other solvent studied. It is soluble to the extent of 23 mole per cent at 25°C. The curve is of the same general shape as the alcohol curves, but at low concentrations of solute it shows greater divergence from the ideal curve and the divergence is in the opposite direction. Its dielectric constant is not of the same order as that of the alcohols, being much lower.

The curve for carbon tetrachloride is rather unusual. It is almost exactly a straight line from 10 to 100 mole per cent of the solute. It is in this respect very different from the alcohols, acetone, and chloroform.

Acetyl-*o*-toluidine was less soluble in ether than in any other solvent studied except water. This curve, while nearly straight, shows slight reverse curvature at about 30 mole per cent. It breaks rather gradually below 15 mole per cent and crosses the carbon tetrachloride curve at 3 mole per cent and the benzene curve at about 1.5 mole per cent.

Acetyl-*o*-toluidine in water gives the phenomena of two liquid phases over a very wide range. It forms two liquid layers at about one-half mole per cent of solute and up to a concentration which has thus far not been determined exactly. No attempt was made to determine the critical solution temperature. The temperature of this triple point is near 79.6°C.

SUMMARY

The synthetic method has been used to determine the solubility of acetyl-*o*-toluidine in methyl alcohol, ethyl alcohol, *n*-propyl alcohol, isopropyl alcohol, *n*-butyl alcohol, isobutyl alcohol, acetone, chloroform, carbon tetrachloride, benzene, diethyl ether, and water.

The heat of fusion of acetyl-*o*-toluidine has been determined, and an ideal solution curve calculated and plotted.

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(5) Reference 3, p. 1839.

STUDIES ON ADSORPTION

THE RELATION OF WATER HELD BY CHARCOAL AT ZERO PRESSURE TO THE ASH CONTENT

L. J. BURRAGE

King's College, London, England

Received May 5, 1933

In the past it has been generally accepted that the quantity of water adsorbed at zero pressure is dependent on the ash content. In the view of the author this is incorrect unless the ash should prove to be definitely hygroscopic. This probably only occurs to a very slight extent even with phosphoric acid activated charcoals, for the charcoal has been activated at a high temperature and most of the hygroscopic salts would therefore fuse, thereby losing this property to a large extent.

As a result of a number of experiments carried out recently, the author is in a position to suggest a more probable theory to account for the varying amounts of water which are held at zero pressure.

EXPERIMENTAL

The charcoals used in the present series which have been previously described are given in table 1. The remainder of the twenty-five charcoals are fully described in table 2.

Samples of these charcoals which had been previously employed in a study of the effect of activation on the isothermal and its relation to water hysteresis (1), were ashed by the following method, which was devised to prevent any loss of ash due to sublimation. The apparatus is shown in figure 1 and consisted of a silica U-tube A, fitted with two ground glass connections, B and C, which were closed by taps.

The general procedure was as follows: The charcoal under examination was heated for 1½ hours in an air oven at 150°C., this temperature being the most suitable for removing the greater part of the adsorbed water without altering the nature of the charcoal surface, and about 2 g. of it was packed into the apparatus, which had been previously cleaned and weighed. The cups D and E were then filled with Everett's wax and the whole reweighed. The charcoal was finally dried by passing dry air at 150°C. through the apparatus at 400 cc. per minute. It was then cooled and weighed. The ashing was carried out in the following manner. The U

TABLE 1

Charcoals used in this series and described previously

CHARCOAL	REFERENCE
A	J. Phys. Chem. **32**, 441 (1928)
B	J. Phys. Chem. **32**, 441 (1928)
C	J. Phys. Chem. **32**, 441 (1928)
D 1	Proc. Roy. Soc. London **130**, 610 (1931)
G	J. Soc. Chem. Ind. **47**, 372 T (1928)
L	J. Phys. Chem. **34**, 2202 (1930)
M 1	J. Phys. Chem. **34**, 2202 (1930)
M 2	J. Phys. Chem. **34**, 2202 (1930)
M 3	J. Phys. Chem. **34**, 2202 (1930)
M 4	J. Phys. Chem. **34**, 2202 (1930)
N	Proc. Roy. Soc. London **132**, 460 (1931)

TABLE 2

Other charcoals used in this study

CHARCOAL	APPARENT DENSITY	STARTING MATERIAL	ACTIVATING AGENT
E 1	0.349	Coal	Steam
F 1	0.534	Coconut shell	Steam
K 1	0.311	Peat	Phosphoric acid
L 1	0.445	Beechwood	Steam
M 5	0.404	Palm nut shell	Steam
M 6	0.392		
M A	0.427	Brazil nut shell	Steam
M B	0.60	Coconut shell	Steam
N 1	0.416	Almond shell	Zinc chloride
P	0.329	Peat	Zinc chloride
Q	0.294	Peat	Zinc chloride
R	0.379	Peat	Steam
S	0.250	Soft wood	Air
T	0.338	Peat	Zinc chloride

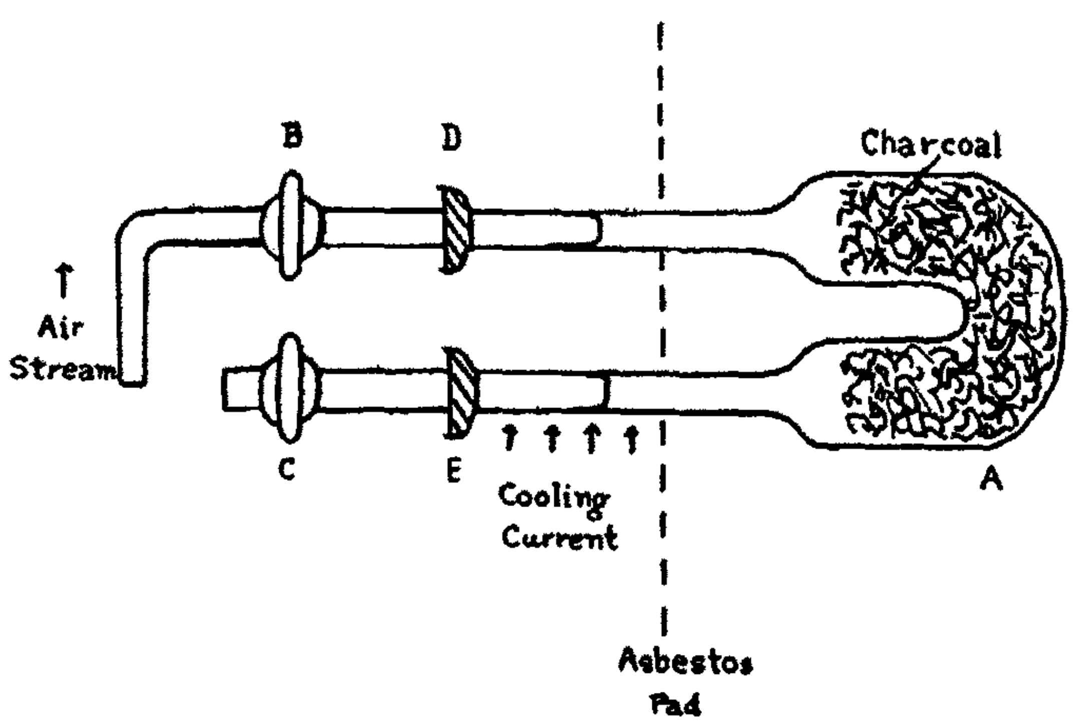

Fig. 1

portion was heated to a bright red heat, the rest of the apparatus being protected by an asbestos pad. Dry air was passed through the limb B at 20 cc. per minute, the exit tube C being cooled with a jet of ice-cold water.

TABLE 3

CHARCOAL	ASH	
	(1)	(2)
	per cent	*per cent*
A	3.98	3.92
N	0.67	0.61
Q	1.65	1.65

TABLE 4

CHARCOAL	PER CENT ASH	WATER AT ZERO PRESSURE	CARBON TETRACHLORIDE AT 0.01 MM. PRESSURE
		milligrams per gram	*milligrams per gram*
A	3.95	15.4	93.0
B	4.03	2.0	57.0
C	2.72	17.5	145.9
D 1	1.81	2.7	116.4
E 1	20.5	2.1	61.0
F 1	3.70	9.0	134.1
G	7.07	2.5	121.9
K 1	27.3	27.1	57.5
L	9.27	18.1	149.7
L 1	6.22	23.8	137.0
M 1	1.17	5.0	4.0
M 2	1.17	26.1	111.6
M 3	1.17	32.9	152.0
M 4	1.17	19.1	143.1
M 5	1.17	19.3	129.6
M 6	1.17	12.2	125.2
M A	6.79	10.1	96.6
M B	1.43	1.0	125.0
N	0.64	12.7	71.4
N 1	0.83	36.3	75.3
P	3.59	2.0	128.5
Q	1.65	10.2	41.9
R	13.1	31.2	122.7
S	3.80	25.2	54.3
T	2.30	25.1	46.0

The ashing was continued until constant weight was attained, the degree of reproducibility of these results being shown by the duplicate experiments (see table 3).

The results of the ash determinations are expressed in table 4, together with the quantities of water held at zero pressure and of carbon tetrachloride at 0.01 mm., which latter results were obtained by employing an air-stream method, in order that as much C_xO_y might be retained on the charcoal surface as possible. In previous work it has been shown that there is excellent agreement between the air stream and vacuum techniques. In this case zero pressure is assumed when there is no loss in weight by passing dry air at 400 cc. per minute for 6 hours. As the water isothermal below 1 mm. is almost parallel to the pressure axis, it follows that the weight figure obtained corresponds to that of zero pressure within experimental error.

DISCUSSION

An examination shows that there is no great variation in the qualitative analysis of the ash of the various charcoals, except in cases where there has been chemical activation or a briquetting agent employed, hence it would appear that there is not sufficient variation in the composition of the ash to account for the various amounts of water which are chemically held.

Again reference to table 4 shows no obvious connection between the ash and the water held at zero pressure. In the series M 1 to M 6, which represents increasing stages of activation, the ash content is constant within experimental error, whereas the quantity of water varies between 5 mg. per gram and 32.9 mg. per gram. Therefore 1 mg. of ash retains 2, 3, 1.5, 1.5, and 1 mg. of water in the cases of M 2, M 3, M 4, M 5, and M 6, respectively. Again N 1 has 36.3 mg. per gram of water tightly held but only 0.83 per cent ash, which would involve 1 mg. ash adsorbing approximately 4.5 mg. of water, sorption of this order being unknown by any substance. In the case of N, 1 mg. of ash adsorbs 2 mg. of water at zero pressure. A sugar charcoal, J, has been found to have 5.4 mg. per gram of water retained at zero pressure (2), although the ash content was 0.1 per cent. This water cannot be retained by the ash, as this would involve 1 mg. of ash adsorbing 5 mg. of water.

Further data have been obtained from the series of measurements on the sorption of water vapor by activated charcoal carried out by Allmand and his coworkers (3). In two experiments carried out with charcoal B, the quantities of water held at zero pressure were 4 mg. per gram by the static and 12 mg. per gram by the air-stream method, the temperature of evacuation, 270°C., being the same in both cases. A comparison of data for charcoals A and C can best be made in tabular form (see table 5), the general trend of which results would be the same if experiments had been carried out at neighboring temperatures.

This is interesting since the ash is 3.95 per cent for A and 2.72 per cent for C, yet the quantities of water fall in the same order under similar conditions. It is impossible to imagine that the same percentage of ash is removed in each charcoal under the same conditions of experiment, which would follow if the water depended on the ash content.

From data such as these it is obvious that the ash content cannot account for the quantity of water held at zero pressure. It has already been shown (4) that water is adsorbed both by the active centers and in a quasi chemical form by the C_xO_y which is always present to a greater or lesser extent on the charcoal surface, the amount depending on the type of charcoal and the treatment to which it has been subjected. This water is held at zero pressure and can only be removed if the C_xO_y complex is broken up. Again the greater the number of active centers on the charcoal surface the greater will be the amount of water held by the free valencies of the exposed carbon atoms, i.e., the greater will be the amount of water tightly held. As a result of a new theory of activation of charcoal (5) it is possible to predict how the water content at zero pressure should alter during the course of a sorption experiment. If a large amount of C_xO_y is present at the commencement a large quantity of water will be sorbed at zero pressure. Some of the more loosely held C_xO_y is slowly removed by the water, thereby causing the quantity of sorbed vapor to drop somewhat. As the C_xO_y is removed from the active points more water will be adsorbed at zero pressure. Hence one would expect a large amount of water to be adsorbed at zero pressure at first, then less, and finally an increased amount again during the course of the experiment. If the bulk of the water is held by the active centers the figures for the amount of water held at zero pressure should bear the same ratio to the carbon tetrachloride figures at 0.01 mm. in each case, since carbon tetrachloride is firmly held at this pressure at room temperature. This was not found to be the case, although the

TABLE 5

Comparison of data for charcoals A and C

METHOD	TEMPERATURE OF EVACUATION	CHARCOAL A	CHARCOAL C
	degrees C.	*milligrams per gram*	*milligrams per gram*
Nitrogen stream	800	44	40
New dynamic*	—	15	18
Nitrogen stream	270	13	14
Static	800	8	10
	270	4	6
NaOH extracted	800	3	2
Oil stream	270		10
	800		23

* Unpublished work by the author.

M 1 to M 6 series shows a definite rise and fall both for water and carbon tetrachloride (table 4). As the result of further work on the sorption of vapor by unactivated charcoal (4) this is an inevitable result, since water can be adsorbed at any active center, on the C_xO_y sponge or at any other point on the charcoal surface, whereas carbon tetrachloride, being a typical non-polar vapor, can only be adsorbed at the active centers. The presence of C_xO_y, which, as has already been stated, is always present to a greater or lesser extent, increases the amount of water sorbed but decreases the quantity of carbon tetrachloride, owing to a poisoning effect. This latter state is shown very markedly when an isothermal on charcoal A, after evacuation at 110°C. (6), is compared with a similar isothermal after evacuation at 800°C. (7). At low pressures the quantity in the latter case is almost twice that of the former, owing entirely to the removal of C_xO_y from the active centers.

TABLE 6

CHARCOAL	APPARENT DENSITY	SAT. Q AT 115 MM.	WATER AT ZERO PRESSURE
		milligrams per gram	*milligrams per gram*
M 1	0.620	12	5
M 2	0.584	376	26
M 3	0.478	682	33
M 4	0.477	729	19
M 5	0.404	892	19
M 6	0.392	920	12

TABLE 7

Comparison of coconut charcoals

CHARCOAL	APPARENT DENSITY	CARBON TETRACHLORIDE Q AT 115 MM.	WATER AT ZERO PRESSURE
		milligrams per gram	*milligrams per gram*
M B	0.60	307	1.0
D 1	0.575	301	2.7
F 1	0.534	424	9.0
C	0.490	647	17.5

In some unpublished work it has been found possible to arrange the charcoals according to the degree of activation, which is the order in which the carbon tetrachloride saturation values fall at 115 mm. at 25°C., the highest figure corresponding to the greatest activation. The data for the series M 1 to M 6 are given in table 6.

This series forms the best for comparison because the starting material is exactly the same in each case, the degree of activation alone being altered. All samples before activation should have more or less the same C_xO_y content. As the latter proceeds, the amount of water held by the active centers will increase, hence the water content at zero pressure should be strictly comparable with the degree of activation, giving a fall followed by a rise.

Finally as the charcoal becomes overactivated the quantity of water will fall.

In table 7 comparison is made between coconut charcoals obtained from different sources. In this case also the agreement is good. One cannot compare data for the briquetted charcoals, which includes all the peat charcoals, as well as L, and L 1, since the degree of compression of the material alters as well as the degree of activation.

SUMMARY

A number of ash determinations have been carried out on different charcoals, and a comparison made with the amounts of water held at zero pressure.

An examination of other available data has been made.

A theory has been advanced to account for this variation in the quantity of tightly held water, in which it has been suggested that the ash plays no part in the retention of the water at zero pressure, but that the latter is held in a quasi chemical manner by the active centers and C_xO_y complex.

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THE SYSTEM SODIUM DISILICATE–SODIUM FLUORIDE

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The ternary system $Na_2O \cdot SiO_2 \cdot NaF$ has been shown to be of fundamental importance in the composition of porcelain (vitreous) enamels. Two of the binary systems contained in the above ternary system have been published, namely, sodium oxide–silica (1) and sodium metasilicate–sodium fluoride (2). This paper describes the study of the system sodium disilicate–sodium fluoride. This is of particular interest to enamelists in view of the suggested use of sodium silicates as a raw material (3), especially since the disilicate contains a high per cent of silica (66.0 per cent) and has a low melting point (874°C.).

The preliminary study (2) of this system showed that difficulties would be encountered owing to the very small heat arrests and the sluggishness of the disilicate in attaining equilibrium. However, by using a special recording potentiometer and supplementing this continuous record with differential readings taken at least every 30 seconds, the breaks could be readily detected. In this way we were able to obtain the data without using the tedious and somewhat less accurate quenching methods.

EXPERIMENTAL PROCEDURE

Chemicals

Some of the silica was obtained from large clear quartz crystals. The foreign matter was scraped off and the crystals boiled in aqua regia. After being thoroughly washed they were placed in a large platinum dish, heated, then suddenly chilled by a stream of cold distilled water. This shattering process was continued until the pieces became small. They were then ground to a powder in an agate mortar.

The other pure silica was from commercial powdered quartz. After a water wash to remove any lint it was boiled three times with hydrochloric acid and twice with aqua regia, followed by a thorough water washing.

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[1] Holder of the Cushman Fellowship for Fundamental Research in Vitreous Enamels, 1930–1931.

[2] Holder of the Cushman Fellowship, 1931–1934.

Both of these samples were then dried in an electric oven at 120°C. On treatment with hydrofluoric acid they gave, respectively, 0.03 and 0.04 per cent residue.

The sodium oxide content was obtained by using C.P. sodium carbonate monohydrate, which by conversion to the sulfate was shown to be 99.90 per cent pure.

Merck's C.P. sodium fluoride was recrystallized twice from water, dried in platinum in an electric oven, and by conversion to the sulfate was found to be 99.00 per cent sodium fluoride. This sample contained 0.80 per cent water.

The sodium disilicate was made by fusing the calculated amounts of sodium carbonate monohydrate and silica in covered platinum crucibles, in a small electric furnace. Since the high viscosity of the disilicate prevented it from being poured, the outside of the crucible was chilled with a stream of cold water. This caused the melt to crack enough so that it could be removed. The material was then ground to a powder in an agate mortar. This was re-fused and re-powdered until it became homogeneous.

Apparatus

The furnace (2) was a vertical resistance furnace, having two windings, an inner one of platinum–20 per cent rhodium alloy wire and the outer of Chromel resistance wire. 110 volts A.C. was used on both coils, the current being controlled by two water-cooled rheostats.

The thermocouple was a standard platinum and platinum–10 per cent rhodium couple. A differential junction surrounded by a platinum-covered nickel "neutral body" of approximately the same heat capacity as the platinum crucible and melt was suspended about 6 cm. above the melting point junction. The melting point crucible was a heavy cylindrical, platinum crucible, 5 cm. high and 1.6 cm. in diameter. The thermocouples and supports for holding the crucible were in a single unit which could be raised and removed from the furnace.

The heating curves were obtained with a specially designed Leeds and Northrup "Micromax" recording potentiometer. This recorder balances every second and has a paper speed of sixteen inches an hour. The temperature can be read to ± 0.5°C. from 500°C. to 1200°C.

The differential temperature readings were made with a "student type" potentiometer and a "wall type" galvanometer. At every reading of the differential temperature a mark was made on the recorder paper by means of an electrically controlled pen. In this way the differential curve could readily be plotted on the recorder sheet.

Preparation and melting points of mixtures

The various mixtures were prepared by weighing out theoretical amounts of the disilicate and sodium fluoride, mixing thoroughly, fusing slowly in a small electric furnace, then chilling rapidly, as mentioned previously. After being ground to a powder each was re-fused and again powdered in order to obtain a homogeneous mixture.

To obtain a melting point, this powder was introduced into the crucible, the thermocouple inserted, and the entire unit placed in the furnace. It was rapidly heated to above the melting point of the mixture, and allowed to cool slowly, so that crystallization could take place. The furnace was then heated again, this time slowly, and both the melt and the differential temperatures were recorded. After the melting point was reached the furnace was again cooled slowly. Only heating curves were taken, as the mixture always undercooled before crystallizing. In every case at least three checks were obtained on both the solidus and liquidus points.

It is difficult to obtain sharp breaks by the usual method of thermal analysis in the sodium disilicate region. However, by carefully controlling the rate of heating of the furnace and taking a continuous melting point record and simultaneously taking the differential readings, the breaks in the heating curve could be easily detected and duplicated. The thermocouple was checked before and after every melting point. The standards used were sodium chloride (800.4°C.) (4) and sodium metasilicate (1089°C.) (1).

In a number of cases the melts, after being used for a melting point determination, were powdered and weighed; definite quantities of either the disilicate or sodium fluoride were then added. The melting points of such mixtures were identical with those of the mixtures of like composition prepared by mixing only the disilicate and sodium fluoride. This indicates that the melt does not change in composition on being fused.

RESULTS

The data obtained are given in table 1 and plotted in figure 1. The system is a simple V eutectic type, no compounds being formed. The eutectic composition is 39.5 ± 0.1 mole per cent of sodium fluoride and the eutectic temperature is 797°C. ± 1°C.

The melting point of the disilicate was found to be 874°C., agreeing with the value obtained by Kracek (1).

The solidus disilicate relations have been shown by Kracek (1) to be very complex. At present the solidus relations for the system sodium disilicate-sodium fluoride below the eutectic temperature have not been studied sufficiently to enable one to draw any definite conclusions.

TABLE 1

The system sodium disilicate-sodium fluoride

POINT NO.	MOLE PER CENT SODIUM FLUORIDE	WEIGHT PER CENT SODIUM FLUORIDE	TEMPERATURES	
			Liquidus	Solidus
			degrees C.	*degrees C.*
1	0.00	0.00	874	
2	10.00	2.50	861	799
3	20.00	5.45	850	796
4	32.52	10.00	825	797
5	39.50	13.09	797	797
6	42.10	14.36	817	799
7	47.04	17.00	870	798
8	53.00	20.64	915	799
9	59.11	25.00	946	796
10	70.00	34.98	973	797
11	81.14	49.80	985	802
12	90.97	69.91	988	793
13	96.06	84.90	991	798
14	100.00	100.00	995	

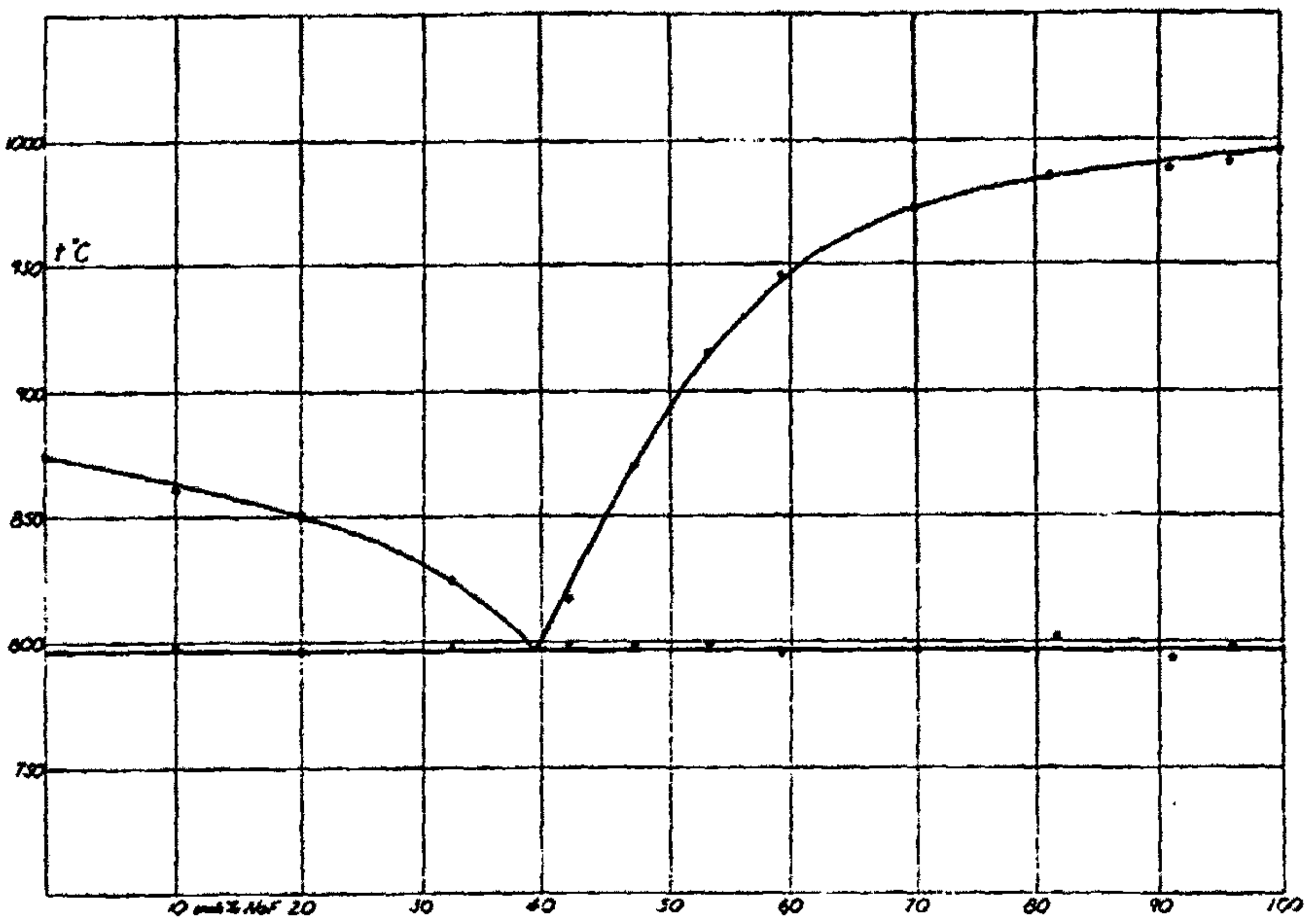

FIG. 1. THE SYSTEM SODIUM DISILICATE-SODIUM FLUORIDE

SUMMARY

The system, sodium disilicate–sodium fluoride, is a one eutectic type and the eutectic occurs at a composition 39.5 ± 0.1 mole per cent of sodium fluoride and at a temperature of 797°C. ± 1.0°C.

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THE CRYSTAL STRUCTURE OF $CaSO_4 \cdot CO(NH_2)_2$

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During the course of studies on salt–urea systems Dr. C. W. Whittaker (1) of this laboratory prepared a well-crystallized material which upon analysis proved to be a urea "coördination" compound of calcium sulfate. Preliminary optical examination showed that the crystals have an unusually high birefringence, approaching that of urea itself. This predicated a sufficiently interesting underlying crystal structure to warrant a thorough study. Considerable importance, moreover, attaches to this compound as one possibly formed in some fertilizer mixtures.

Crystal structure determinations of a number of hydrates and ammoniates have shown the essential validity of Werner's coördination theory as applied to polar, but uncharged, groups. No attempt, however, has yet been made to find the structure of a coördination compound containing urea, ethylene diamine, or pyridine, etc. This hesitancy has been well based on the knowledge that these large molecules might place insuperable barriers in the way of the analyst and leave him with nothing more than a space group determination for his efforts.

The analysis of urea coördination compounds holds some hope when the importance of the inherently high anisotropy of the urea molecule is fully realized. In the case of $CaSO_4 \cdot 4CO(NH_2)_2$ the optical properties proved to be an unerring guide through the complexities of an unusually complex triclinic crystal. The structure found is perhaps sufficiently accurate to serve as the basis of a future more elaborate analysis. It holds some additional interest in being the first triclinic ionic compound to have yielded its essential crystal structure.

CRYSTALLOGRAPHIC AND OPTICAL PROPERTIES

In general the crystals were elongated prisms (0.5 x 0.5 x 1 mm.) showing predominant development of the p faces, figure 1, with only the forms a, b, c, p_1, and p_2 present. Two crystals with the x faces developed were measured on the optical goniometer. The results together with the calculated crystallographic constant are given in table 1.

A small fraction of the crystals were found to be twinned on (001). One specimen was measured on the universal stage under the microscope. The spherical projection of the twin axis was obtained from the point of intersection of the three great circles connecting in order the projections of the principal directions of the optical ellipsoids of the two crystals. The twin axis was found to be either the *b* axis or the normal to the *b* face. A second specimen, giving moderately bright signals from the *p* faces, was measured on the optical goniometer. The results, which are summarized in table 2,

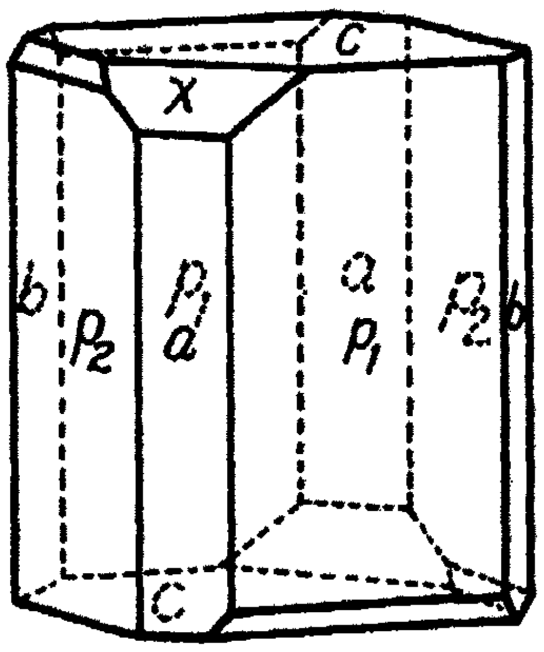

FIG. 1. A TYPICAL CRYSTAL OF $CaSO_4 \cdot 4CO(NH_2)_2$

TABLE 1

Goniometric measurements

FORM		ρ	φ	LIMITS OF OBSERVATIONS		FACES MEASURED
				ρ	φ	
100	*a*	90°1′	93°12′	90°0′ to 90°2′	93°12′ to 92°56′	4
110	p_1	90°2′	47°3′	90°0′ to 90°2′	47°2′ to 47°4′	4
010	*b*	90°1′	00°0′	90°0′ to 90°2′	359°50′ to 0°10′	4
$\bar{1}10$	p_2	90°0′	136°10′	90°0′ to 90°0′	136°7′ to 136°10′	4
001	*c*	2°9′	9°58′	2°4′ to 2°14′	9°56′ to 9°60′	2
101	*x*	41°30′	90°39′	41°28′ to 41°32′	90°35′ to 90°43′	2

$\nu = 93°9'$ $\mu = 89°45'$ $\lambda = 87°53'$
$\alpha = 92°6'$ $\beta = 90°22'$ $\gamma = 86°50'$

$$p_0 : q_0 : r_0 = 0.8796 : 0.8658 : 1$$
$$a : b : c = 0.9836 : 1 : 0.8645$$

Clear signals were obtained only from forms p_1 and p_2. These were accordingly given infinite weight in calculating ν and p_0'/q_0'. The value of α is particularly sensitive to ρ for 001 and therefore is likely to be considerably in error.

Forms observed *a*, (100), *b* (010), *c* (001), p_1 (110), p_2 ($\bar{1}10$), *x*, (101), ($1\bar{1}1$), (111), ($\bar{1}\bar{1}1$), ($\bar{1}11$), ($\bar{1}01$).

Cleavage absent.

The face development indicates that the crystals are holohedral.

show that the twin axis is the crystallographic *b* axis and that the composition plane is (001). A number of crystals apparently twinned in other manners were examined on the universal stage and in every instance were shown to be either parallel growths or unrelated crystals closely adhering to one another.

The indices of refraction measured under the microscope by the immersion method for Na_D light are at 25°C.:

$$\alpha = 1.523, \beta = 1.583, \gamma = 1.615$$

The experimental error does not exceed ±0.002. The crystals are optically negative with $2V$, calculated, 70.0°.

TABLE 2

Goniometric measurements on a twinned crystal mounted on $(00\bar{1})$

The V scale has been inverted to agree with the previous crystallographic description

FORM		ρ	φ	FACES
Crystal No. 1				
$\bar{1}10$	p_2	90°2′ to 90°4′	136°9′ to 136°10′	2
010	b	90°0′ to 90°4′	359°45′ to 359°46′	2
110	p_1	90°4′ to 90°6′	47°1′ to 47°7′	2
100	a	90°4′ to 90°0′	92°40′ to 92°57′	2
Crystal No. 2				
110	p_1	88°55′ to 89°00′	315°20 to 315°22′	2
010	b	87°57′ to 88°3′	358°53′ to 359°13′	2
$\bar{1}10$	p_2	88°14′ to 88°16′	46°16′ to 46°19′	2
100	a	89°40′ to 90°22′	93°9′ to 93°13′	2

The measurements on ρ of the two members of the same form are reduced to comparable values. Signals, not very clear, were obtained only from forms *p*.

The orientation of the optical ellipsoid was determined by measurements on the universal stage. The crystals were mounted in an ethylene glycol-phthalic anhydride plastic between hemispheres with $n_D = 1.557$. The average results, uncorrected for differences in refractive indices, obtained from a number of crystals are summarized in figure 2. The irregular lines indicate the magnitude of the observational errors. The observed value of $2V$ is 70°, agreeing with the value calculated from the indices of refraction.

X-ray diffraction data

Rotating crystal and Weissenberg photographs were made with the crystallographic axes as axes of rotation. Copper *K* radiation was used throughout with a camera radius of 5.01 cm.

The lattice dimensions were calculated from the layer line separations. The angles between the axes of the reciprocal lattice and the values of p_0, q_0, and r_0 were determined from the equatorial zone Weissenberg photographs. The linear elements calculated from these measured quantities are listed in table 3. The values obtained from the x-ray diffraction and optical goniometric data agree very closely save in the case of α, in which instance the goniometric value is suspect.

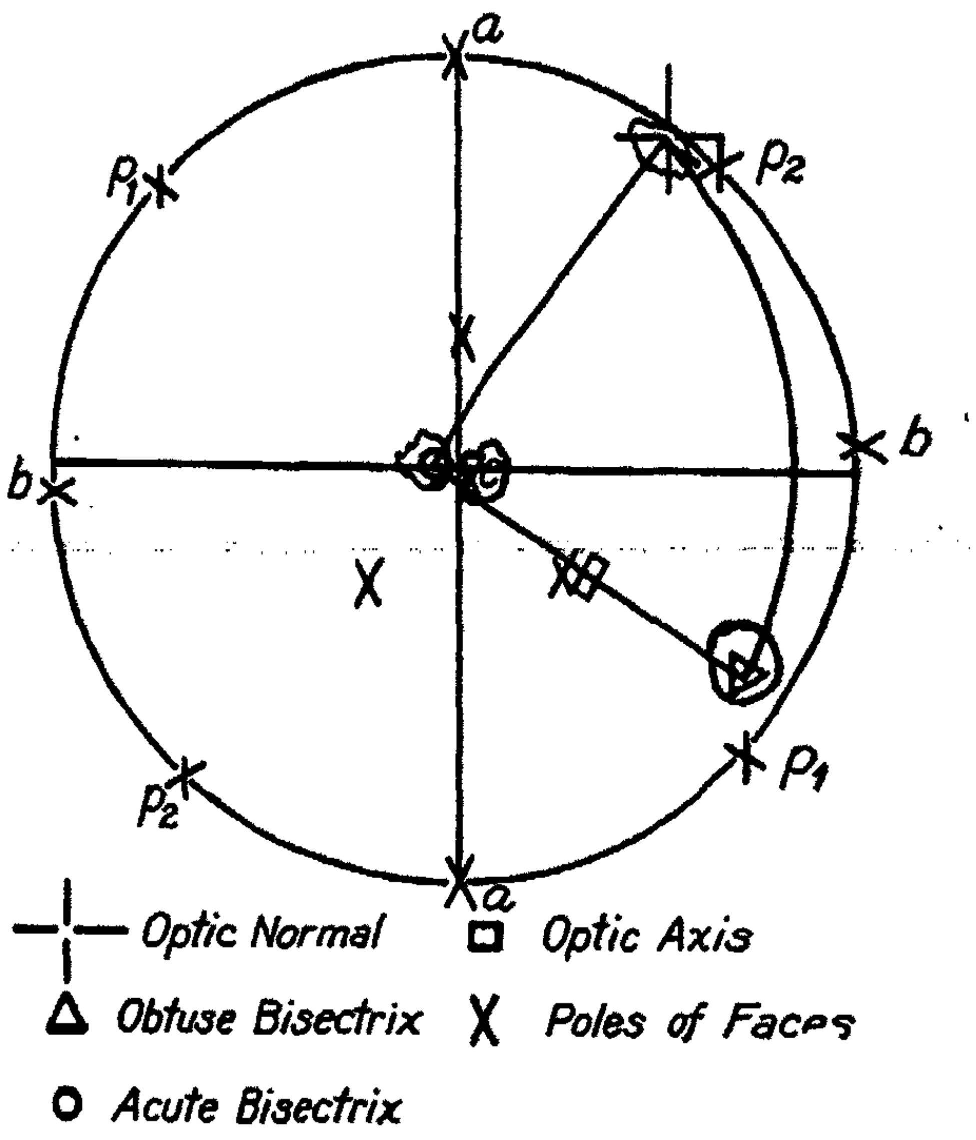

FIG. 2. STEREOGRAPHIC PROJECTION SHOWING THE OPTIC ORIENTATION OF $CaSO_4 \cdot 4CO(NH_2)_2$ AS DETERMINED ON THE UNIVERSAL STAGE

The projection of the c axis is at the center of the figure

Weissenberg photographs were made from four of the layer lines. In these cases the slit was rotated making $\sin \beta = \sin \mu$ (2) so that the axis of rotation would lie on the reflection sphere. The absence of symmetry around the central image confirmed the triclinic character of the crystals.

The intensities of some of the observed reflections are summarized in tables 4 to 9. *A most striking characteristic of these data is that many types of planes are either absent or are represented by only a few of the possible reflections.* The observations can be divided into two classes (σ denotes odd; e, even):

Strictly absent	*Approximately absent*
$(\sigma 00)$, $(0\sigma 0)$	(00σ)
$(\sigma e0)$, $(e\sigma 0)$	$(\sigma\sigma 0)$
$(0\sigma l)$, $(\sigma 0l)$	$(0k\sigma)$, $(h0\sigma)$
$(e\sigma l)$, (σel)	$(ee\sigma)$, (σoe)

The data from Weissenberg photographs of the third and fourth layer lines are summarized in tables 7 and 8. It can be seen that reflections are

TABLE 3

Summary of crystallographic constants

	WEISSENBERG X-RAY	GONIOMETER OPTICAL
a_0 from layer	14.74	
b_0 line	14.95	
c_0 separation	6.47	
γ^*	93°18′	93°9′
α^*	88°36′	87°53′
β^*	89°42′	89°45′
α	91°26′	92°8′
β	90°22′	90°22′
γ	86°42′	86°50′
p_0	0.4395	0.8796
q_0	0.4326	0.8658
r_0	1	1
a	0.9859	0.9836
b	1	1
c	0.4327	0.8645
Density (observed)	1.8006	
Density (calculated)	1.820	

TABLE 4

Weissenberg photographic data from $CaSO_4\cdot 4CO(NH_2)_2$

Equatorial zone, *a*, axis of rotation. All planes with *k* odd are strictly absent; the only reflections from planes with *l* odd are listed in table 9

	$0k2$	$0k4$	$0k6$	$0k\bar{2}$	$0k\bar{4}$	$0k\bar{6}$
$00l$	v.s.*	v.w.	v.w.	v.s.	v.w.	v.w.
$02l$	s.	a.	w.	?	v.w.	m.w.
$04l$	m.s.	m.s.	m.w.	m.s.	m.	m.w.
$06l$	w.	m.w.	w.	m.w.	w.	m.w.
$08l$	m.	m.	v.w.	m.	m.	w.
$0.10.l$	m.	w.	a.	m.	m.w.	
$0.12.l$	m.w.	m.		m.w.	m.w.	
$0.14.l$	m.w.	m.w.		v.w.		
$0.16.l$	w.	w.		w.		

* The following abbreviations are used: v.s., very strong; s., strong; m.s., medium strong; m., medium; m.w., medium weak; w., weak; v.w., very weak.

present only from ($\sigma\sigma\sigma$), ($ee\sigma$), and ($\sigma\sigma e$). Weissenberg photographs were made from the second layer lines with c and with b as the axes of rotation. Complete indices were not assigned in these cases, since positive and negative values were not differentiated, but it could be seen that planes ($\sigma21$), ($e\sigma2$), and ($\sigma e2$) were strictly absent and ($e2\sigma$), ($\sigma\sigma2$) approximately so. Laue photographs were made with the incident beam (W general radiation, 26,000 V peak) parallel and at slight angles to the b axis. Reflections in the first order ($n\lambda$ = 0.48 to 0.96 A.U.) were obtained only from ($\sigma\sigma\sigma$),

TABLE 5

Weissenberg photographic data from $CaSO_4 \cdot 4CO(NH_2)_2$

Equatorial zone, b, axis of rotation. All planes with h odd are absent; the only reflections from planes with l odd are listed in table 9

	$h02$	$h04$	$h06$	$h0\bar{2}$	$h0\bar{4}$	$h0\bar{6}$
$20l$	m.s.	m.	v.w.	s.	a.	v.w.
$40l$	m.	m.	m.w.	m.	m.	w.
$60l$	m.w.	m.w.	m.	w.	m.	v.w.
$80l$	m.s.	m.	m.w.	w.	m.w.	w.
$10.0.l$	m.s.	v.w.	a.	m.w.	a.	
$12.0.l$	w.	w.		m.w.	w.	
$14.0.l$	w.			m.w.		
$16.0.l$	m.					

TABLE 6

Weissenberg photographic data from $CaSO_4 \cdot 4CO(NH_2)_2$

Equatorial zone, c, axis of rotation. All planes with h or k odd are absent save the few h and k odd listed in table 9

	$0k0$	$2k0$	$4k0$	$6k0$	$8k0$	$10.k.0$	$12.k.0$	$14.k.0$
$h00$		v.s.	s.	a.	m.s.	v.w.	v.w.	m.w.
$h20$	v.s.	m.	m.	a.	w.			
$h40$	m.s.	v.s.	m.s.	m.	a.			
$h60$	w.	w.	m.s.	v.w.	a.			
$h80$	s.	a.	m.	m.	m.			
$h.10.0$	w.	a.	a.	v.w.	m.	m.		
$h.12.0$	w.	v.w.	m.w.	m.	m.			
$h.14.0$	a.	m.w.	w.					
$h.16.0$	m.w.	w.						
$h\bar{2}0$		m.	v.s.	w.	a.	a.	w.	m.w.
$h\bar{4}0$		m.s.	m.s.	m.s.	m.	v.w.	m.	w.
$h\bar{6}0$		a.	m.	m.w.	m.w.	m.	m.	
$h\bar{8}0$		m.w.	a.	m.w.	m.	m.s.	v.w.	
$h.\bar{10}.0$		a.	w.	v.w.	w.	w.	w.	
$h.\bar{12}.0$		a.	m.w.	m.w.	m.w.			

($ee\sigma$), and ($\sigma\sigma e$), without particular differentiation in intensities between the three classes.

The odd layer lines on the rotating crystal photographs, while present in all cases, are far less prominent than are the even ones. Some strong reflections are present on the odd layer lines however, particularly for values of ξ less than 1.2. Some of these characteristics can perhaps be seen by an inspection of the typical photograph reproduced as figure 3.

TABLE 7

Weissenberg photographic data from $CaSO_4 \cdot 4CO(NH_2)_2$

Fourth layer line, a, axis of rotation. All planes with k odd are strictly absent; the only reflection from planes with *l* odd are listed in table 9

	$4k2$	$4k4$	$4k\bar{2}$	$4k\bar{4}$	$4\bar{k}2$	$4\bar{k}4$
$40l$	m.	m.w.	m.s.	m.	m.	m.w.
$42l$	v.w.	w.	w.	m.w.	m.s.	v.w.
$44l$	s.	w.	s.	m.w.	s.	w.
$46l$	m.s.	a.	w.	a.	m.w.	v.w.
$4.8.l$	w.		m.w.	a.	m.w.	m.w.
$4.10.l$	a.		a.		a.	w.
$4.12.l$	m.w.		m.w.		w.	

TABLE 8

Weissenberg photographic data from $CaSO_4 \cdot 4CO(NH_2)_2$

Third layer line, *a*, axis of rotation. All planes with *k* even are strictly absent

$3\bar{1}0$ a.	310 a.	$3\bar{1}1$ v.w.		311 v.s.	$31\bar{1}$ s.
$3\bar{3}0$ v.w.	330 a.	$3\bar{3}1$ v.w.	$33\bar{1}$ a.	331 a.	$33\bar{1}$ a.
$3\bar{5}0$ w.	350 w.	$3\bar{5}1$ v.w.	$3\bar{5}1$ a.	351 m.	$35\bar{1}$ w.
370 v.v.w.	370 v.w.	371 v.w.	$37\bar{1}$ w.		$37\bar{1}$ a.
$3\bar{9}0$ w.	390 a.	$3\bar{9}1$ m.w.	$3\bar{9}\bar{1}$ w.		
$3.\bar{11}.0$ a.			$3.\bar{11}.\bar{1}$ a.		
$3.\bar{13}.0$ a.	$3\bar{1}2$ w.		312 w.	$3\bar{1}3$ w.	313 a.
$3.\bar{15}.0$ w.	$3\bar{3}2$ m.s.	$33\bar{2}$ w.	332 m.	$3\bar{3}3$ v.w.	333 w.
	$3\bar{5}2$ a.	$35\bar{2}$ m.w.		$3\bar{5}3$ w.	
	372 a.	$37\bar{2}$ a.			
	$3\bar{9}2$ a.			$3\bar{1}4$ w.	315 w.
	$3.\bar{11}.2$ w.				

Although unambiguous index assignments can only be made for Weissenberg and Laue photographs it can nevertheless be seen that none of the reflections of greater than medium intensity on the odd layer lines with *a* and *b* as axes of rotation had close to the same values of ξ as reflections on the two adjacent layer lines. Since the values of the angles, α, β, and γ are very close to 90° it follows that the planes giving reflections on the odd layer lines in general have different values of *h* and *l*, or of *k* and *l* than those present on the even layer lines. This then would be compatible with the presence chiefly of planes $(\sigma\sigma e)$ and $(\sigma\sigma\sigma)$, as borne out by the Weissenberg photographs of the layer lines. The subduing of the odd layer lines with *c* as the axis of rotation can be explained in the same manner.

The density calculated on the basis of the unit of structure containing four $CaSO_4 \cdot 4CO(NH_2)_2$ is 1.820. This value agrees with that determined by the centrifugal suspension method, 1.8006. The 1 per cent discrepancy arises chiefly from errors in the values of the fundamental lattice constants.

The space group is either $P1$, or $P\bar{1}$. The face development and the character of the signals indicate that the crystals belong to the holohedral division of the triclinic system. The derived structure, although isomorphous with $P\bar{1}$, does not depend upon the assumption of holohedry.

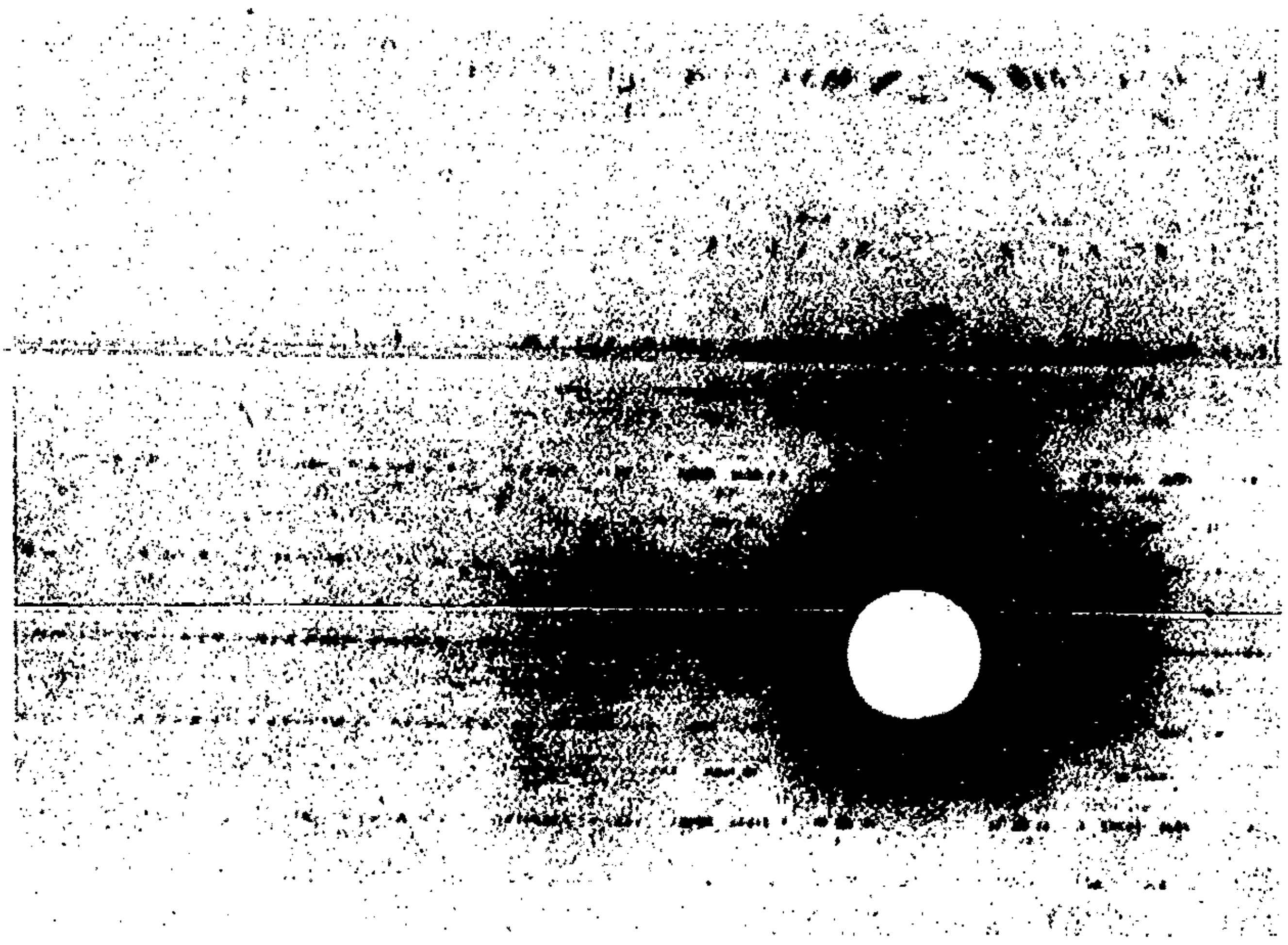

FIG. 3. ROTATING CRYSTAL PHOTOGRAPHS
Copper *K* radiation; *a* axis of rotation

THE STRUCTURAL AND OPTICAL PROPERTIES OF CALCIUM SULFATE AND UREA

The crystal structure of anhydrite, $CaSO_4$ (3), is known with sufficient accuracy to show that eight oxygen ions of sulfate groups are in the first coördination sphere around each calcium ion. In gypsum (4), as described at the present time, each calcium ion is surrounded by four oxygen ions of sulfate groups and two water molecules of closest approach. In calcium oxide and in the various silicates containing calcium the coördination number for oxygen ions has been found to be six, seven, or eight.

The most trustworthy value for the Ca^{++} to O^{--} distance for a coördination number of six is 2.40 A.U., as found for calcium oxide. For coördinations of 4 to 8 this value would be expected to be between 2.25 and 2.55 (5). The values observed in the various calcium silicates are close to 2.40, usually between 2.35 and 2.55. The sulfur to oxygen distance has not yet been determined in a sulfate. It is quite safe to assume, however, that it is the same as the phosphorus to oxygen distance in KH_2PO_4 (6), namely, 1.56 A.U., and that the oxygen ions are at the corners of regular tetrahedrons surrounding the sulfur ions.

The described structure of gypsum is of questionable accuracy since the calcium–oxygen distances are as small as 2.1 A.U. and since the first coördination sphere around calcium contains but six oxygen atoms, of which only four are ions. The structure is perhaps sufficiently accurate to indicate that the water molecules are near the calcium ions, the distances as given being 2.40 A.U. Consideration of a number of ammoniates and hydrates suggests that such polar groups approach to within about 2.80 A.U. of calcium ions, the limits of this value being very wide

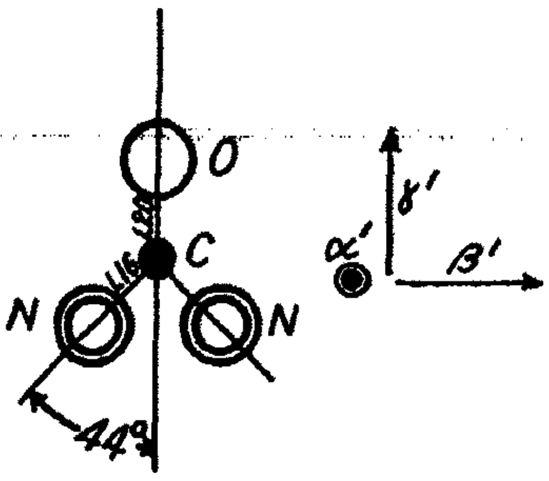

FIG. 4. THE INTERATOMIC DISTANCES IN A UREA MOLECULE

The centers of all the atoms are in the same plane. The directions of maximum, mean, and minimum polarizations are shown.

Inspection of the crystal structure of urea shows that the oxygen ends of the molecules are near the NH_2 groups of other molecules. The closest intermolecular distances of approach are: O to NH_2, 3.15 A.U. The properties of urea indicate that its molecules are polar, the NH_2 groups being positive with respect to the oxygen atoms.

In general the birefringence of sulfates R_2SO_4, RSO_4, or $R_2(SO_4)_3$ is low, since a regular tetrahedral grouping of isotropic resonators, such as afforded by a SO_4 group, is isotropic. The indices of refraction of anhydrite, $CaSO_4$, are $\alpha = 1.571$, $\beta = 1.576$, $\gamma = 1.614$, with the density, ρ equal to 2.93. In gypsum $\alpha = 1.520$, $\beta = 1.523$, and $\gamma = 1.530$ with $\rho = 2.32$. The birefringence of calcium sulfate formed by dehydrating gypsum at low temperatures is less than 0.015.

Urea crystallizes in the tetragonal system with $\alpha = \beta = 1.484$, $\gamma = 1.602$, and $\rho = 1.335$. The direction of maximum polarization is parallel to the twofold axes of the molecules. α and β are perpendicular to the plane of half the urea molecules and parallel to the planes of the other half. The optical properties of a lattice formed by the translation repetition of urea molecules can not satisfactorily be calculated at the present time. It is sufficient however to indicate, as permitted by elementary considerations, that α', β', and γ' would have the directions shown in figure 4, with β' somewhat smaller than γ' and α' very small compared to β' or γ'.

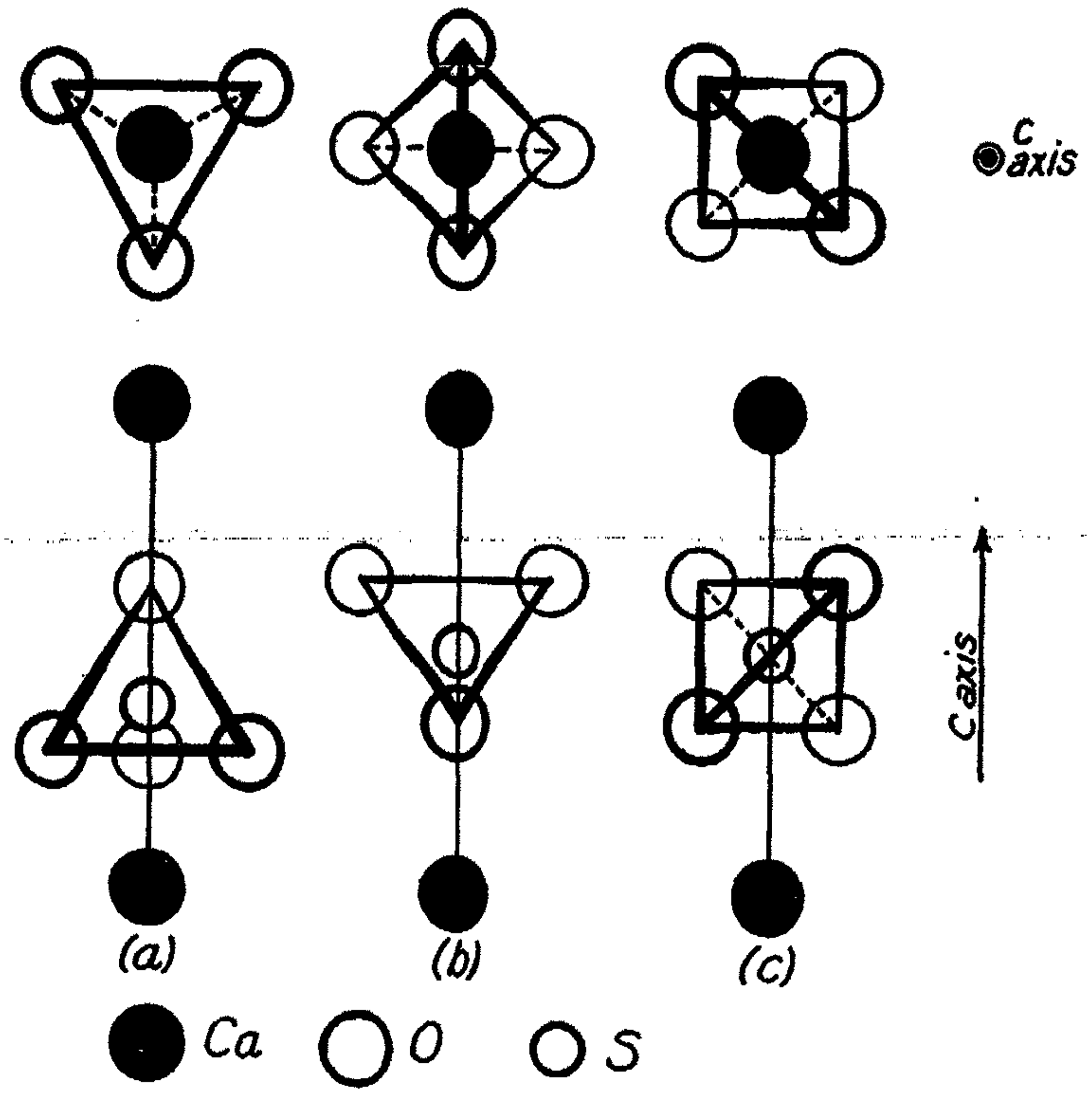

Fig. 5. Possible Arrangements of the Ca^{++} Ions and SO_4 Groups along the c Axis of $CaSO_4 \cdot 4CO(NH_2)_2$

Rotations about the c axis are not determined. The calcium–oxygen distances are (a) 2.43 A.U., (b) 2.64 A.U., and (c) 2.68 A.U.

The crystal structure of $CaSO_4 \cdot 4CO(NH_2)_2$

The explanation of the many types of absent reflections affords the starting point for the structure determination. The lattice must approach very closely to being a face-centered one, particularly in the *a* and *b* directions. Each atom must have approximate translations of 000; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$. The calcium atoms can be placed in these positions without loss in generality.

The regular tetrahedral sulfate groups having sulfur to oxygen distances equal to 1.56 A.U. are to be placed within this lattice of calcium ions, in a manner such that the Ca^{++} to O^{--} distances are about 2.40 A.U. Fortunately, there are but three ways in which this can be accomplished. These are shown in figure 5 The arrangement shown in figure 5a gives interatomic distances in better agreement with expectation than do the other two.

TABLE 9

Weissenberg photographic data from $CaSO_4 \cdot 4CO(NH_2)_2$

Reflections observed from (*eeσ*) and (*σσe*)

EQUATORIAL ZONE *a*, AXIS OF ROTATION		EQUATORIAL ZONE *b*, AXIS OF ROTATION		EQUATORIAL ZONE *c*, AXIS OF ROTATION	
(021) w.	($0\bar{2}1$) m.s.	($20\bar{1}$) w.	(201) v.w.		(330) v.w.
(041) m.	($0\bar{4}1$) m.	($40\bar{1}$) m.s.	(401) m.w.		($\bar{1}50$) w.
(081) m.w.	($0.\overline{12}.1$) v.w.	($60\bar{1}$) v.w.	(10.0.1) v.w.	(150) w.	($\bar{5}50$) v.w.
(0.16.1) m.	($0.\overline{14}.1$) w.		(12.0.1) m.w.	(350) v.w.	($\bar{7}50$) v.w.
	($0.\overline{16}.1$) w.	($00\bar{3}$) v.w.	(14.0.1) v.w.		($\bar{9}70$) v.w.
(003) v.w.	($0.\overline{18}.1$) w.	($20\bar{3}$) w.			(390) v.w.
(063) m.w.		($60\bar{3}$) m.	(12.0.3) w.		($\bar{5}90$) v.w.
(0.16.3) m.	($0.\overline{10}.3$) v.w.	($12.0.\bar{3}$) w.			($\bar{9}.11.0$) w.
	(0.12.3) *m.*				
(0.14.5) w					
FOURTH LAYER LINE *a*, AXIS OF ROTATION					
($40\bar{1}$) m.s.	(401) m.				
($4\bar{2}1$) m.s.	($4\bar{4}1$) w.				
($44\bar{1}$) w.	($4.\overline{10}.1$) v.w.				
($46\bar{1}$) w.	($4.\overline{12}.1$) w.				
(441) m.s.					

The arrangement of figure 5b will be used as the basis for later drawings, but none of the possibilities must really be considered as excluded. In none of the cases do considerations of distances alone fix the group in its rotation around the *c* axis. In no instance can both the symmetry of the point group $P\bar{1}$ and the complete translations of a face-centered lattice be maintained. The arrangements 5b and 5c will, however, preserve the face centering in the *a* and *b* directions, and that of the sulfur atoms in the *c* direction. They appear somewhat more reasonable for this reason, as well as on account of the arrangements they give oxygen ions around the calcium ions. In any case the calcium ions are equidistant from four oxygen ions of closest approach. Strong electrostatic forces are effective in holding the lattice together in the *c* direction only.

It is somewhat instructive to consider the twinning in crystals of gypsum, anhydrite, and $CaSO_4 \cdot 4CO(NH_2)_2$. In general the composition plane of a twinned crystal is one across which the electrostatic binding forces are great and in which the atoms are brought into approximate juxtaposition by rotation about the twin axis. In gypsum and anhydrite the composition plane and twin plane are the same and contain only sulfate groups or calcium ions, (101) of anhydrite and (100) of gypsum, or sulfate groups and calcium ions, (012) of anhydrite. These are all planes across which the binding forces are relatively great. The twinned crystals of $CaSO_4 \cdot 4CO(NH_2)_2$ thus might be expected, as observed, to have (001) as the composition plane.

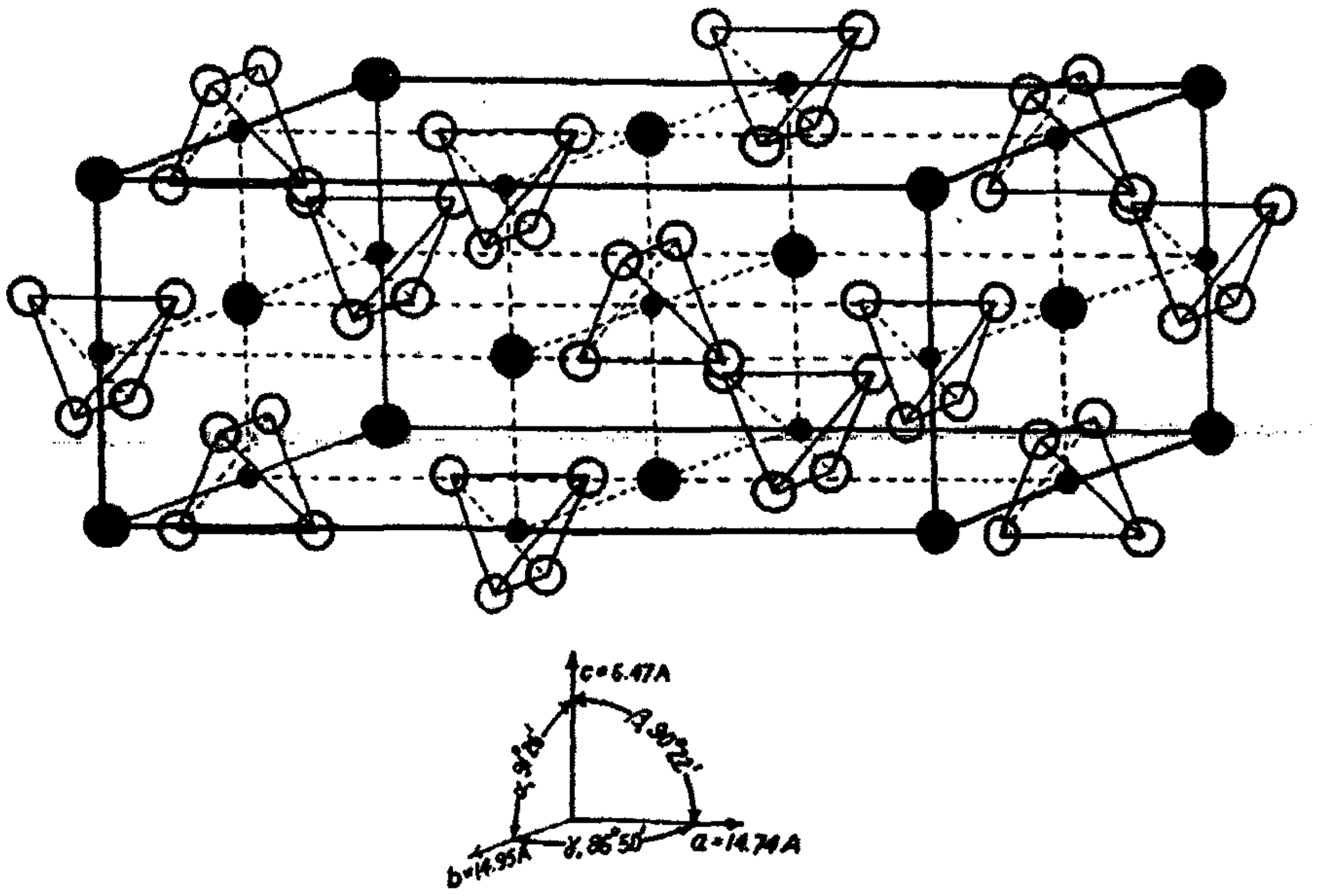

FIG. 6. ARRANGEMENT OF THE Ca^{++} AND SO_4^{--} IONS IN THE UNIT OF STRUCTURE OF $CaSO_4 \cdot 4CO(NH_2)_2$

The birefringence of $CaSO_4 \cdot 4CO(NH_2)_2$, which is almost as great as that of urea, is to be explained by the arrangement of the urea molecules in its structure. These molecules, moreover, must be placed with their oxygen ends near positive charges, calcium ions, and their NH_2 groups near negative ions, the oxygen atoms of the sulfate groups. The lack of prominent cleavage allowed by the calcium sulfate framework is prevented by the urea arrangement. The interatomic distances mentioned in the last section must be satisfied approximately as must also the fundamental face-centered translations.

Since the direction of *a* does not differ greatly from that of *c* the planes of urea molecules can not deviate widely from being perpendicular to *c*. This would also require the obtuse bisectrix and the optic normal to be in (001) with the polarizations along them not greatly different.

A manner, and apparently the only one, of satisfying these manifold requirements is that shown in figures 6 and 7. The undetermined factors in this approximate structure are (1) the exact positions of the sulfate groups and their rotations around the *c* axis, and (2) the details involved in fixing the positions of the urea molecules, chiefly translations.

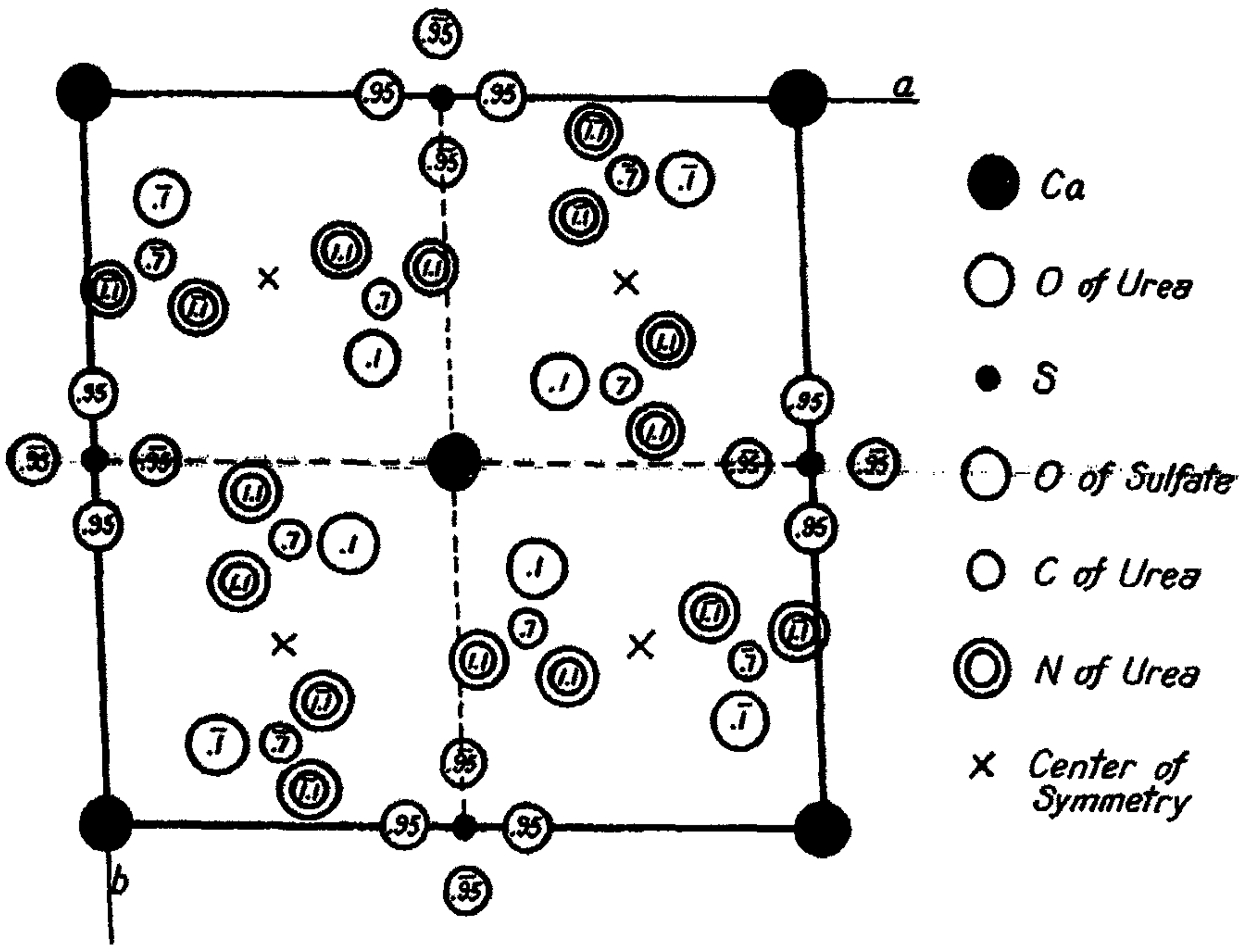

FIG. 7. A PROJECTION OF ONE HALF THE UNIT OF STRUCTURE ON (001)₀

The distances of various atoms above and below the plane are shown. The projection on (001)½ is obtained by translating the origin of this figure to $x = \frac{1}{2}$, $y = 0$. The unit of structure can be formed by the combination of the two projections.

The structure is complete enough to show qualitative agreement between observed and calculated intensities of reflection for simple planes. The various types of absences are accounted for, but of course not in a unique manner. The observed intensities and calculated structure factors for low order reflections from the pinacoids are:

(200) v.s. (020) v.s. $A/4 = F_{Ca} + F_S + 2.9F_{O\text{ of }SO_4} + 1.2F_{O\text{ of }CO(NH_2)_2} - 1.4F_C - 2.8F_N$

(400) s. (040) m.s. $A/4 = F_{Ca} + F_S + 0.7F_{O\text{ of }SO_4} - 3.2F_{O\text{ of }CO(NH_2)_2} + 0.4F_C + 3.2F_N$

(600) a. (060) w. $A/4 = F_{Ca} + F_S - 3.6F_C + 0.7F_N$

(800) m.s. (080) s. $A/4 = F_{Ca} + F_S + 1.6F_{O\text{ of }SO_4} + 1.2F_{O\text{ of }CO(NH_2)_2} + 2.6F_C - 0.6F_N$

(001) a. $A/4 = O$

(002) v.s. $A/4 = F_{Ca} + F_S + 3.9F_{O\text{ of }SO_4} - 1.0F_{O\text{ of }CO(NH_2)_2} + 0.8F_C - 4.0F_N$

(003) v.w. $A/4 = O$

(004) v.w. $A/4 = F_{Ca} + F_S + 3.7F_{O\text{ of }SO_4} - 3.6F_{O\text{ of }CO(NH_2)_2} - 3.8F_C - 3.4F_N$

Moreover it is to be noted that the intensities of *hk*0 for *h* and *k* less than 8 are approximately symmetrical and independent of sign, as would be required by the indicated structure.

CONCLUSIONS

The crystallographic and optical constants of triclinic crystals of $CaSO_4 \cdot 4CO(NH_2)_2$ have been measured. Analysis of x-ray diffraction data led to a partial determination of the crystal structure which is shown in figures 6 and 7.

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PHOTOCHEMISTRY OF FLUORESCEIN DYES[1]

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It is well-known that the fluorescein dyes photosensitize the oxidation of readily oxidizable substances by molecular oxygen (Gaffron, 1926; Carter, 1928). Several investigators have shown that peroxide is formed under proper conditions when the dyes are irradiated in solutions which do not contain readily oxidizable substances (Weigert, 1912; Gaffron, 1926; Blum, 1930). The nature of the peroxide has not been clearly shown and the question as to whether it represents an intermediate step in the oxidative process has not been definitely settled. In the following study an attempt has been made to determine the nature of the peroxide formed when fluorescein dyes are irradiated in aqueous solutions (Weigert, 1912; Blum, 1930). Four possible sources for the peroxide have been considered: (1) impurities present introduced in the preparation of the dye, (2) the dye itself, (3) breakdown products of the dye, since the dye is bleached concomitantly with the formation of peroxide, (4) water, resulting in the formation of hydrogen peroxide.

EXPERIMENTAL

The first possibility was tested by preparing fluorescein from very pure intermediates, resorcinol and phthalic anhydride, and purifying carefully by recrystallization. The fluorescein was dissolved by the addition of an equivalent amount of sodium hydroxide, made up to 10^{-3} M and irradiated in a thin layer with a 200-watt tungsten filament lamp at a few centimeters distance. After irradiation for about twenty hours, such solutions contained up to 10^{-3} N hydrogen peroxide, as determined iodometrically. Since the concentration of peroxide formed is of the order of that of the dye, it is highly improbable that it should be a peroxide of any impurities present.

Rate studies

It was thought that simultaneous studies of the rates of bleaching and of peroxide formation should be of value in differentiating between the other three possibilities mentioned above. Such studies offer considerable diffi-

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[1] This investigation was assisted by a grant from the Board of Research of the University of California.

culties, since it is necessary to use fairly intense irradiation over considerable periods of time in order to obtain measurable quantities of peroxide. The method finally adopted was to irradiate successive samples with the same source, a given 200-watt tungsten filament lamp, for varying periods, analysis for peroxide and determination of the degree of bleaching being made for each sample at the end of the irradiation period. Figure 1 is a rate curve obtained in this way. The samples consisted of 100 cc. of a 0.00028 M solution of eosin[2] in distilled water, this concentration being

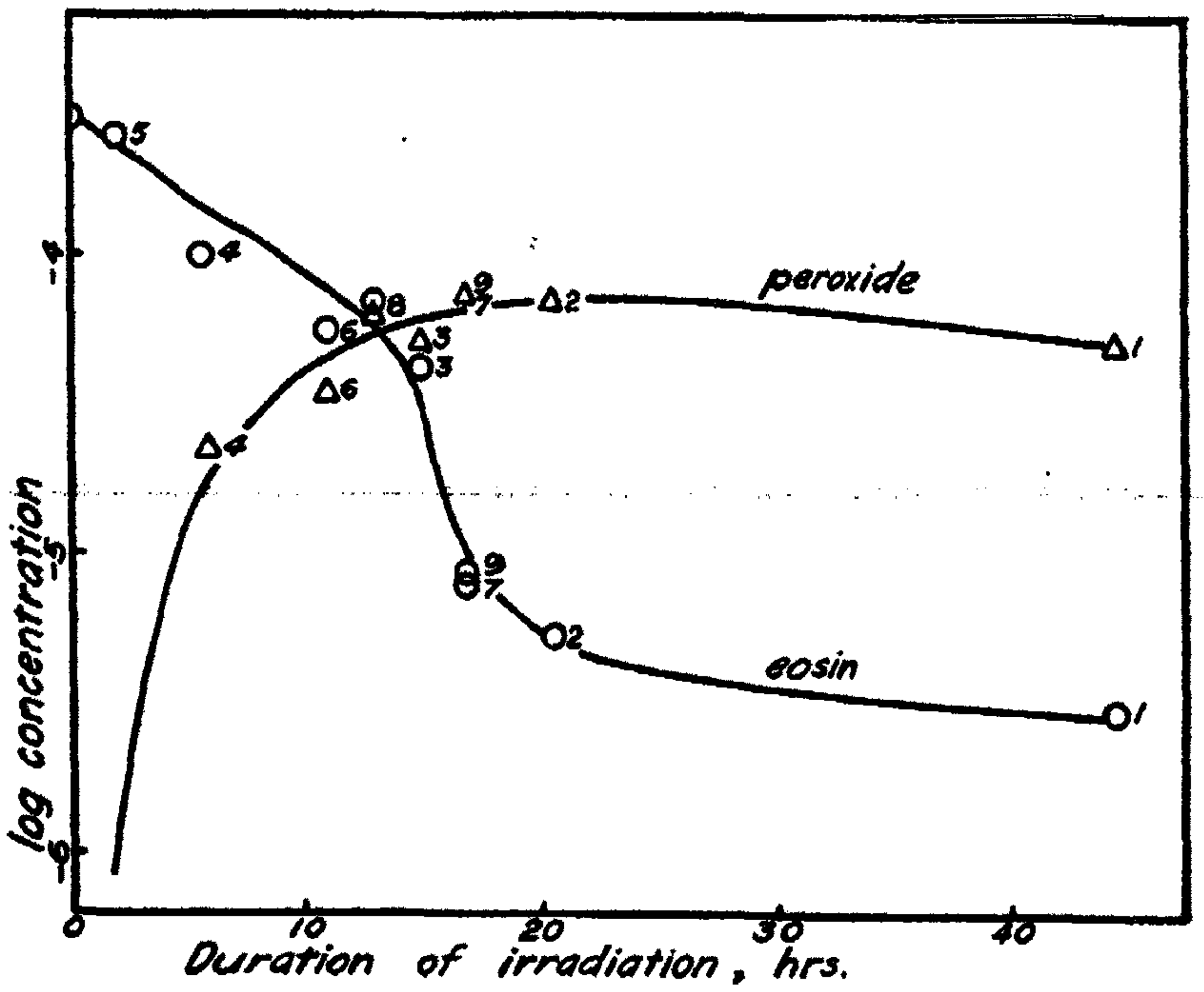

FIG. 1. RATE OF BLEACHING AND PEROXIDE FORMATION FOR IRRADIATED EOSIN

Dye concentrations are in moles per liter; peroxide concentrations in equivalents per liter. Numbers of points indicate the order of the determinations. At 2 hours (point 5) a test for peroxide was obtained, but the quantity was too small for accurate titration.

selected for convenience in analysis. These samples were placed in a 1000-cc. Erlenmeyer flask, forming a layer approximately 1 cm. thick on the bottom of the flask and supported at a distance of approximately 7 cm. above the filament of an ordinary 200-watt Mazda lamp; the distance between the lamp and the flask was carefully reproduced for each sample. The system was cooled by a blast of air directed across the bottom of the

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[2] Eosin Y (sodium salt of tetrabromofluorescein) from Coleman and Bell.

flask above the lamp bulb; temperatures were maintained in this way between 32°C. and 33°C. after the first half hour of irradiation. The scheme has the advantage that the solution is irradiated in a fairly thin layer, which is of importance since oxygen is a necessary component of the reactions and has a very definite effect on their rate (see Weigert, 1912, and below). Provision for shaking to establish uniform distribution of oxygen was found impracticable because of frothing of the dye solution. It was found difficult to obtain sufficiently intense irradiation for volumes of solution large enough to provide for the removal of aliquots adequate for analysis, and such a method is subject to the objection that the thickness of the layer of solution is altered upon the removal of each aliquot.

The scheme has the disadvantage that the rates are subject to variations in the intensity of emission of the source which definitely varies with the age of the lamp, the extent of this variation being different for different lamps. Some of our determinations were found to be untrustworthy because of this, but the curve shown in figure 1, all the points of which were obtained with the same lamp, seems to be free from this objection. That the intensity of the irradiation did not greatly alter in this case is indicated by the accuracy with which certain of the determinations could be duplicated, and that the points obtained in random order (indicated in the figure) fall on definite curves. Furthermore, the general shape of the dye-concentration curve, i.e., having a sharp break downward at about the time maximum peroxide concentration is reached, was found to be typical of all the curves obtained. The break occurred later with less intense irradiation.

The dye concentrations were determined spectrophotometrically. Although Beer's law does not hold exactly for the fluorescein dyes (see Pringsheim, 1928, p. 226), it was found by determining the absorption of various dilutions of eosin at 5200 A. U., approximately the maximum absorption of eosin, that the law could be applied safely for the concentrations at which our determinations were made. Since some shifting in the absorption spectrum of eosin occurs upon irradiation (see Wood), the absorption spectra of a certain number of irradiated samples were determined; these appear in figure 2. It will be seen from this figure that any shift in the region of maximum absorption is not of great importance in these cases, nor do the curves appear greatly affected by the presence of colored breakdown products. Thus it seems safe to use the absorption at 5200 A. U. as an index for calculating the concentration of dye in the irradiated samples; it is probably more correct to consider the concentrations so obtained as maximum dye concentrations, since in the cases of extreme bleaching the presence of breakdown products would probably tend to increase the total absorption.

The photo-compound described by Wood (1922) on the basis of absorption spectrum measurements was studied in the case of fluorescein, but does not appear to play an important part in the reactions herein discussed. It is not formed in the absence of oxygen, but is not a reversible oxidation, since there is no return to the original color when reducing substances are added, hence it is not a peroxide of the dye. It may represent a first step in the oxidative bleaching of the dye. Eosin was used in our rate determinations because the shift in the absorption spectrum is less pronounced than in the case of fluorescein, and therefore the determinations of concentration should be more accurate.

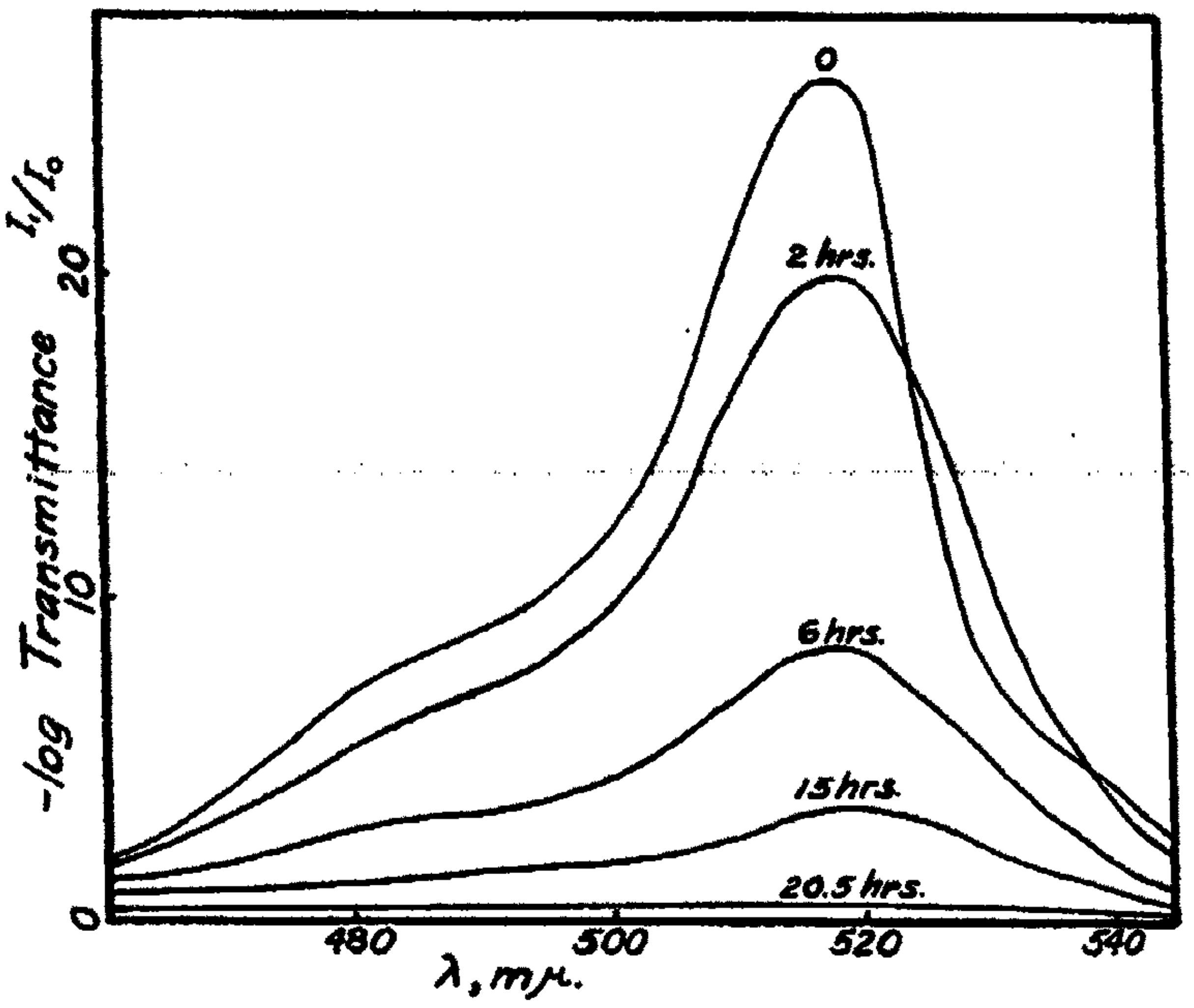

Fig. 2. Absorption Spectra of Irradiated 0.00028 *M* Eosin

0 = non-irradiated dye. Calculations based on absorption of 1 cm. thickness of solution. Higher concentrations diluted 1 to 10 for analysis.

The following method was found satisfactory for the determination of peroxide in the small quantities with which we were dealing. Approximately 2 g. of potassium iodide was placed in a 100-cc. volumetric flask with 5 cc. of 6 *N* hydrochloric acid and about 70 cc. of water. The sample to be analyzed, usually about 20 cc., was added by pipette and the mixture made up to volume. After standing for 30 minutes, the contents of the flask were emptied into a 500-cc. Erlenmeyer flask and titrated with 0.001 *N* sodium thiosulfate against starch indicator. The sodium thiosulfate was prepared frequently by dilution from a standardized 0.1 *N* solution. The end point is sometimes difficult because of the presence of the dye precipitate formed when the acid is added to the dye solution, but the error from this source is not great. The method was checked by titration of solutions of known hydrogen peroxide concentration diluted to the same approximate concentrations as those of our irradiated dye samples, both with and without the addition of non-irradiated dye. The error was estimated as within 5 per cent at the lowest peroxide concentrations at which determinations were attempted; at higher concentrations it was much less. One source of error is the oxidation of iodide ion by atmospheric oxygen, resulting in high values for hydrogen peroxide; this is avoided by keeping the solution in the narrow necked volumetric flask during the 30 minute period before the titration.

The rate curves (figure 1) are subject to certain definite criticisms. Hydrogen-ion concentration was not controlled, because of the fact that electrolytes slow the reaction and hence it was found impracticable to use buffers. The oxygen tension was likewise not controlled for the reasons mentioned above. Both these factors may have an influence on the shape of the rate curves. Nevertheless two facts stand out quite distinctly. After a considerable period of irradiation, the concentration of peroxide may reach a value considerably greater than that of the dye remaining in the solution, e.g., in figure 1 beyond 20 hours the concentration of peroxide is, mole for mole, at least five times as great as the concentration of dye, and thus at least a great part of the peroxide would have to be present in some other form than dye peroxide. The increase of peroxide does not appear to show any direct relationship to the destruction of the dye, indicating that the peroxide is not a compound of breakdown products of the dye.

Behavior of the peroxide

These facts point toward the fourth of the possibilities outlined above, namely, that the peroxide formed upon irradiation of the dyes is hydrogen peroxide. Comparison of the behavior of this peroxide with hydrogen peroxide was therefore made.

Separation of the peroxide from the dye. If the peroxide is hydrogen peroxide it should be possible to separate it from the dye; it was found possible to accomplish this by precipitating the dye as its acid or as an insoluble lake by the addition of Ag^+. When a strong acid (say 0.1 N hydrochloric acid) is added to a sample of an irradiated fluorescein dye, the dye is precipitated and can be filtered off. If a filtrate thus prepared was analyzed for peroxide, it was found to contain quantitatively the same amount as a sample from which the dye had not been separated. When the precipitate was redissolved with sodium hydroxide and acidified, no trace of peroxide could be detected.

When silver nitrate is added in excess to an irradiated fluorescein dye solution, the dye is precipitated as an insoluble lake. After centrifuging to throw down the lake, removing the Ag^+ from the decanted solution by the addition of sodium chloride, and filtering, it was found that over 80 per cent of the peroxide appeared in the filtrate, and no trace in the precipitate. Similarly, when a dye solution to which hydrogen peroxide had been added was treated in the same manner, approximately the same percentage of peroxide was recovered in the filtrate. Fluorescein, eosin, phloxin,[3] and erythrosin[4] all gave similar results.

The chromic acid reaction. This test depends upon the formation of the blue perchromic acid, which may be separated from the aqueous solution because of its solubility in ether. The test is subject to certain difficulties which are discussed by Noyes, Bray, and Spear (reference 6, p. 545). The procedure used by us was as follows: 100 cc. of a 0.001 *M* solution of eosin was irradiated for 15 hours, at the end of which time a 20-cc. sample of the solution was titrated iodometrically for peroxide, a concentration of approximately 0.001 *N* being found. Five cc. of 6 *N* nitric acid was added to 50 cc. of this solution. This precipitated the dye, which was filtered off. To the acid filtrate in a 125-cc. Erlenmeyer flask was added 5 cc. of pure ether, forming a layer a few millimeters thick on the surface of the liquid. Two blanks, one consisting of 50 cc. of the unradiated dye solution, and one of 50 cc. of this solution plus 5 cc. of 0.01 *N* hydrogen peroxide, were prepared in the same way. Four cc. of approximately 0.01 *N* potassium chromate was added to each of the above mixtures. The irradiated dye and the blank containing hydrogen peroxide showed a distinct decolorization of the yellow chromate ion, when compared with the blank without hydrogen peroxide, with a faint blue color in the ether layer when viewed from the side through the total thickness of the layer. The ether layer in the blank remained colorless. The intensity of the blue color was comparable in the irradiated dye sample and the hydrogen peroxide blank. From this test, we may conclude that the irradiated dye solution, so treated, contained a concentration of hydrogen peroxide approximately the same as that in the blank, namely 0.001 *N*, which compares favorably with the figure for the iodometric titration.

Rate of reduction by hydrogen iodide. The rate of reduction of our peroxide by hydrogen iodide was studied as follows: Titration of five 20-cc. samples from 100 cc. of 0.001 *M* irradiated eosin were made at varying intervals after adding 4 cc. of 6 *N* hydrochloric acid and 4 g. of potassium iodide to each sample. The intervals covered a period of 30 minutes and provide data for a rate curve for the reduction of the peroxide with hydrogen iodide. Sodium thiosulfate (0.001 *N*) was used for the titration. At the end of 30 minutes the curve had reached a constant value, indicating

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[3] Dichlorofluorescein.

[4] Tetraiodofluorescein.

a peroxide concentration of approximately 0.001 N. Samples of 0.001 N hydrogen peroxide and 0.001 N hydrogen peroxide plus 0.001 M eosin were similarly treated. The rate curves for the three solutions were identical within the limits of accuracy. Since the rate of reduction of the peroxide in the irradiated dye sample is the same as that of hydrogen peroxide, there can be little doubt that the peroxide is the same.

Decomposition by catalase. In all the above tests, except the separation of the dye by means of Ag^+, it was necessary to acidify the solution in the course of the procedure, and it is possible that such treatment might bring about the formation of hydrogen peroxide from an existing organic peroxide. The decomposition by catalase was studied in the attempt to avoid this possibility. Catalase is known to decompose hydrogen peroxide at a rapid rate, whereas it does not, so far as has been studied, decompose organic peroxides or peroxyacids at a perceptible rate (Stern, 1932). Catalase was prepared from liver according to the method described by Waksman and Davidson (reference 11, p. 253). When 5 cc. of the catalase mixture was added to 25 cc. of irradiated dye solution containing approximately 10^{-3} N peroxide, the decomposition of the peroxide occurred rapidly at a rate comparable with the decomposition of a similar solution of hydrogen peroxide. When the catalase was inhibited by adding 5 cc. of 10 per cent sodium cyanide to like samples, decomposition of the peroxide did not occur, indicating that the above decomposition was due to the catalase and not to reduction of hydrogen peroxide by reducing substances which might have been present in the catalase mixture.

The above experiments indicate that hydrogen peroxide is formed, and since the quantity bears no direct relation to the quantity of dye or of breakdown products, it is reasonable to assume that it is formed from water and oxygen. The following energy calculations show that this is possible. The principal reaction involved would appear to be:

$$2H_2O\ (l) + O_2 \rightarrow 2H_2O_2\ (aq);\ F_{298} = 50{,}180 \text{ calories};\ H = 46{,}000 \text{ calories}^{5} \qquad (1)$$

This gives a thermal equilibrium concentration of hydrogen peroxide of about 10^{-18} M (Lewis and Randall, reference 4, pp. 596–7). In agreement with this we found that a dye solution showed no measurable peroxide formation in the dark over a two week's period. On the other hand, the hydrogen peroxide concentrations of the order of 10^{-3} M formed in the light indicate we are dealing with a purely photochemical reaction, and not, for example, a thermal chain reaction initiated by light.

Lacking experimental evidence, no scheme will be offered here for the intermediate steps necessary in the above reaction. It is possible that a

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[5] The data for the calculation of F and H in this paper were obtained from Lewis and Randall (1923). The values of H are taken to the nearest 1000 calories, which is sufficient for our purposes.

dye peroxide may be formed, but if so, it must break down very rapidly to hydrogen peroxide and dye.

The value of 46,000 calories for ΔH is equivalent to a quantum with wave length 6195 A.U.,[6] and this represents the maximum wave length which may bring about this reaction. The absorption spectra of the fluorescein dyes in the visible region are included below this wave length. It is understood that this maximum wave length is only approximate, since some molecules will contain energy greater than the mean value and may be raised to the necessary level by smaller quanta.

The reaction:

$$2H^+ + O_2 = H_2O_2\ (aq);\ \Delta F = -31{,}470\ \text{calories} \tag{5}$$

has a large negative free energy but could not account for the concentration of hydrogen peroxide formed in our experiments, since the concentration of H^+ limits the concentration of hydrogen peroxide which can be formed to $10^{-14}\ M$.

The mechanism:

$$\begin{gathered} D + O_2 = 2O + D;\ \Delta H = 128{,}000\ \text{calories}^7 \\ H_2O + O = H_2O_2 \end{gathered} \tag{6}$$

is, likewise, ruled out since reaction 6 would require 128,000 calories, which represents a maximum wave length of less than 3000 A.U., to which our vessel is opaque.

Some energy of activation would be required to forward reaction 1, and if this were high, the maximum wave length must have a considerably lower value. Unfortunately the data for calculating this energy of activation is not available; it might be greatly reduced by intermediate steps.

The mechanism of bleaching

The bleaching which occurs concomitantly with peroxide formation is not the reduction of the dye to its leuco base, as is shown by the fact that the color does not return when oxidizing agents are added. While this bleaching reaction has been treated as a separate reaction above, we have obtained evidence that it is dependent upon peroxide formation: (1) In the absence of oxygen neither bleaching nor peroxide formation occurs, e.g., a solution of 0.000614 M eosin was irradiated for 5 hours in an evacuated flask, evacuation being carried sufficiently low to boil off some of the water. At the end of the irradiation the volume of solution was found to be 15 per cent reduced owing to the evacuation, its concentration being 0.00074 M eosin. This agrees within the limits of accuracy with a concentration of

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[6] See Taylor (reference 9) for calculation.

[7] Value from Mecke (1929).

the dye by a reduction of volume of 15 per cent, i.e., 0.00072 *M*. (2) When a readily oxidizable substance (sodium thiosulfate) is present which may react with the peroxide, bleaching is greatly inhibited, e.g., a sample of 0.0006 *M* eosin was bleached over 99 per cent during 12 hours irradiation, a sample containing the same concentration of dye plus 0.025 *N* sodium thiosulfate was bleached less than 20 per cent during a like period of irradiation. In the latter case sodium thiosulfate was oxidized in quantity corresponding to 0.005 equivalent per liter, a quantity equivalent to approximately four times the peroxide concentration equivalent mole for mole to that of the dye originally present. This indicates that the quantity of peroxide formed has no direct relation to the quantity of dye bleached. These facts indicate that the bleaching is not a direct decomposition of the dye molecule following the absorption of a quantum of energy, as does also the fact (see figure 1) that the rate of bleaching in the absence of oxidizable substance other than the dye, is not a straight line function of the number of molecules present.

As mentioned above, a dye solution remaining in the dark for two weeks formed no peroxide; no bleaching had occurred in the same time. A similar solution containing 10^{-3} *N* hydrogen peroxide likewise showed no bleaching, but a decrease in peroxide concentration comparable to that of a similar hydrogen peroxide solution without dye. Similarly, an irradiated dye solution shows a slow decrease in peroxide concentration if maintained in the dark for some hours after irradiation, but no bleaching of the dye. The behavior of the peroxide in the irradiated dye solution is, thus, similar to that of hydrogen peroxide, i.e., it does not react with the dye in the absence of light.

On the other hand, hydrogen peroxide rapidly bleaches the dye in strongly alkaline solution. This suggested the possibility that the reaction between hydrogen peroxide and dye may be activated by light, and it was found that dye solution containing hydrogen peroxide bleaches much more rapidly in light than does a similar dye solution without hydrogen peroxide, e.g., 0.0006 *M* eosin plus 0.005 *N* hydrogen peroxide bleached 40 per cent in 4 hours; a similar dye solution without hydrogen peroxide bleached only 15 per cent in the same time with the same light source. The activation of the reaction by hydroxyl ion may be considered as due to the reduction of the energy of activation of this reaction; the activation by light as due to the supply of the necessary energy of activation by a light quantum absorbed by the dye molecule. The latter would be more probable than that the hydrogen peroxide molecule is activated by light, since hydrogen peroxide does not absorb appreciably in the spectral region supplied by our light source (Urey et al, 1929). Such a mechanism might readily explain the shape of our rate curve (figure 1). The formation of hydrogen peroxide and the oxidation of the dye by hydrogen peroxide would both be dependent upon the absorbed radiation. The second reaction, being dependent upon the first, would proceed much more rapidly as the hydrogen peroxide concentration was increased, which would account for the S-shaped curve. Such an explanation would also account for the findings of Wood (1922) whose experiments must have been conducted under conditions similar to ours, i.e., without control of hydrogen-ion concentration or oxygen tension. Wood found that a solution of fluorescein bleached more rapidly when a small portion of it was subjected to concentrated radiation, than when the same quantity of radiation was distributed over a larger surface. In the first case the break in the rate curve would occur earlier than in the second. We actually found that the break occurred earlier with more intense radiation; and if taken at the proper time, the solution subjected to the more intense radiation would show the greater bleaching. Wood suggested that his results were due to the fact that each dye molecule must absorb two quanta of energy before the decomposition occurs; this assumption is not necessary to explain the facts if the above scheme is adopted.

Inhibition by oxygen

Weigert (1912) has shown that peroxide formation is inhibited by high partial pressures of oxygen. We have found that when the oxygen tension is raised from 0.2 atmosphere (air) to one atmosphere, peroxide formation and bleaching are both inhibited for a time. The same treatment inhibits the oxidation of a readily oxidizable substance (sodium thiosulfate) when photosensitized by eosin. The nature of this inhibition is not clear and no hypothesis will be offered at the present time.

SUMMARY

1. The peroxide formed when fluorescein dyes are irradiated in aqueous solution is probably hydrogen peroxide.

2. It is suggested that the bleaching of the dyes by light is an oxidation of the dye by the hydrogen peroxide, this reaction requiring activation of the dye molecule by light.

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A STUDY OF SEVERAL REACTIONS OF CARBON TETRACHLORIDE SYNTHESIS

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INTRODUCTION

The manufacture of carbon tetrachloride, mainly for use as a grease solvent or as a fire extinguisher, is a relatively important industry. In 1925 the value of the output had reached the million dollar mark. Owing to its advantageous properties, the demand for carbon tetrachloride would undoubtedly increase if its price could be decreased. A glance at current prices shows carbon tetrachloride at about 6 cents per pound in drums and chlorine at below 2 cents in tank cars. There would seem to be much advantage in the discovery of a process of manufacture of carbon tetrachloride superior to the old carbon bisulfide chlorination process now in use.

The whole field of the chemistry of carbon tetrachloride is very dark, and what illuminated spots there are, are quite unattached. As will be recalled, the direct synthesis of carbon tetrachloride has not been successfully carried through, commercially. Theoretically there seems to be no reason why this synthesis does not take place readily. Recently both Bodenstein and Stock have been working on this subject, without obtaining results which were satisfactory either commercially or theoretically. The present study was instituted to investigate this field further and to attempt to help toward the clearing up of the situation.

The principal problems in our carbon tetrachloride research are the difficulty with which carbon tetrachloride forms and the difficulty with which its presence can be detected when at a low partial pressure in related gases. The difficulty of formation might be explained by steric hindrance (1). Practically all of the proposed schemes studied involve one reaction step which cannot at present be carried out practically, regardless of the free energy change. This is usually, but not always, the step in which the carbon tetrachloride is finally produced. Of course, the problem may be merely that of finding the proper catalysts, which no one has definitely discovered in spite of many trials. However, it also has the appearance of something more complicated, possibly the "false equilibrium" which Duhem describes (2) so thoroughly. This phenomenon seems to be found so far in the following reactions, proceeding from either side,

$$C + 2Cl_2 = CCl_4 \qquad (1)$$
$$2COCl_2 = (COCl_2)_2 \qquad (2)$$
$$2COCl_2 = CO_2 + CCl_4 \qquad (3)$$

and probably in

$$C_2Cl_6 + Cl_2 = 2CCl_4 \qquad (4)$$

Hood's explanation for the second reaction (3) is that the catalyst was poisoned by phosgene, but he did not investigate the phenomenon further.

Owing to the absence of simple and reliable methods for analysis of the small amounts of carbon tetrachloride that might be obtained in its formation reactions, the decomposition reactions have been studied much more widely, in fact, almost entirely. Arcs, sparks, visible and ultraviolet light, and heat with various catalysts have been some of the means employed. The principal reactions that we will consider are the following; they are gas phase or gas–solid interface reactions.

$$C + 2Cl_2 = CCl_4$$
$$C_2Cl_6 + Cl_2 = C_2Cl_4 + 2Cl_2 = 2CCl_4$$
$$2COCl_2 = CO_2 + CCl_4$$

They may all proceed simultaneously, but something has been learned about their catalysts and reaction temperatures, so that each has been studied separately. It is very difficult to study their reaction rates quantitatively, and this has not been attempted by anyone as yet. These three reactions will be considered under separate headings.

In the present research pure and dehydrated chemicals were not used, as it was desired to study conditions that might be commercially obtained. Another item is that stopcocks were never greased, but were well ground and practically gas-tight, and the apparatus was run at slightly over atmospheric pressure. Any thermodynamic data taken from the literature and for which we have not given the source have been obtained from the International Critical Tables (4).

We have been working in what appears to be a very large field. Accordingly, it has not been possible to allow to any of the reactions investigated a sufficient amount of study to carry it to anything like a logical conclusion. However, we plan to continue study of these reactions, particularly the first and third mentioned above.

THE SPECIFIC HEAT OF CARBON TETRACHLORIDE VAPOR

No instance has been found in the literature of the direct determination of the molar specific heat at constant pressure of gaseous carbon tetrachloride. Capstick (4) determined the ratio of the specific heats as 1.13 at 20°C., which, on using Berthelot's relationship (5) for their difference,

$$C_p - C_v = R\left(1 + \frac{27\, pT_c^3}{16\, p_c T^3}\right)$$

yields for the value of C_p, 17.7 calories per mole at 0.1 atmosphere. Applying the correction for pressure, as will be later outlined, to obtain the value at 1 atmosphere, the result is 18.4 calories. Owing to its magnitude with respect to R, C_p calculated from Capstick's data is probably inaccurate. Furthermore, we have no indication of the slope of the relationship between C_p and T. Therefore we decided to calculate C_p for the vapor at 1 atmosphere. For temperatures below the boiling point this condition would be merely hypothetical, but the results just as useful. We employed the following equation, which can be derived exactly by thermodynamics (6):

$$C_p(g) = C + \frac{dL}{dT} - \frac{L}{T} + T\left(\frac{dV}{dT}\right)_p \frac{dp}{dT} + B$$

C is the specific heat of the liquid under its saturated vapor, L is the heat of vaporization under saturation conditions, $\left(\frac{dV}{dT}\right)_p$ is for the vapor at the saturation pressure, and B is a term to convert C_p from the saturation pressure to 1 atmosphere. The value of B is determined as follows (6):

$$\left(\frac{dC_p}{dp}\right)_T = -T\left(\frac{d^2V}{dT^2}\right)_p ; \; B = T\int_1^p \frac{d^2V}{dT^2}\,dp$$

Since there are insufficient actual experimental data, Berthelot's equation of state was assumed to hold closely enough for the calculation of this correction term. Several simplifications were necessary to avoid tedious computations, involving mainly introduction of the perfect gas law for reduction of the smaller terms. The final result is:

$$B = -\left.\frac{6R^4T^4}{RT(R^3T^4 - ap) + 2abp^2}\right]_1^p$$

where a and b are the Berthelot constants, which in terms of the critical point data are given as

$$a = 16/3\; p_c V_c^2 T_c \text{ and } b = V_c/4$$

The value of C was obtained from Hirn's and from Regnault's results (7), and is expressed by

$$C = 30.5 + 0.0209t + 0.000205t^2$$

giving calories per mole in terms of degrees Centigrade. L we obtained from the published data. $\mathrm{d}L/\mathrm{d}T$ we calculated by passing a cubic equation in T through four selected values of L. By differentiation,

$$\frac{\mathrm{d}L}{\mathrm{d}T} = -59.17 + 0.316T - 0.000518T^2$$

To obtain $T(\mathrm{d}V/\mathrm{d}T)_p$, Berthelot's equation in the form

$$pV = RT\left(1 + \frac{9pT_c}{128p_cT}\left(1 - 6\frac{T_c}{T}\right)^2\right)$$

is differentiated, giving as the desired quantity

$$T\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_p = \frac{RT}{p} + \frac{108RT_c^3}{128p_cT^2} = 0.082\left(\frac{T}{p} + \frac{3,245,200}{T^2}\right)$$

This quantity is in liters, for p in atmospheres. Owing to the complexity of the $p - T$ relationship as shown by the data of Young (4), $\mathrm{d}p/\mathrm{d}T$ was not obtained directly, but was calculated by the Clapeyron-Clausius equation

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L}{T(V_g - V_l)} = \frac{0.26794L/T}{\frac{1}{d_g} - \frac{1}{d_l}}$$

in atmospheres per degree Centigrade for carbon tetrachloride. The figures calculated by this equation agree very well with differences from Young's data. His density data were used. For the point at 20°C. the empirical equation, to be discussed later, was employed:

$$\log p_{\mathrm{mm.}} = 7.8717 - \frac{1732}{T}$$

C_p was calculated up to 280°C., although it was expected that at the higher temperatures it might be unreliable. The critical temperature is 283°C. The results of the calculations are shown in table 1. The values of C_p have been plotted in figure 1. The straight line curve which we have drawn through the points appears to us to be the most probable locus of the true values. Its equation is:

$$C_p = 14.0 + 0.0233T$$

Certainly the accuracy cannot be high, owing mainly to uncertainties in dL/dT, C, and $(dV/dT)_p$, particularly at the two or three temperatures, but the graph is a useful indication, and is probably not in error by more

TABLE 1

Calculation of C_p of carbon tetrachloride(g) at 1 atmosphere

t	dp/dT	$T\left(\frac{dV}{dT}\right)_p$	$-L/T$	dL/dT	$T\left(\frac{dV}{dT}\right)_p \frac{dp}{dT}$	C	B	$C_p(g)$
degrees C.	*atmospheres per degree C.*	*liters*	*calories per degree C.*	*calories per degree C.*	*calories per degree C.*	*calories per degree C.*	*calories per degree C.*	*calories per degree C.*
20	0.00557	196.6	−26.52	−11.07	26.70	30.97	0.68	20.8
80	0.03301	28.38	−20.12	−12.17	22.72	33.46	−0.04	23.9
120	0.0734	11.97	−16.53	−15.01	21.35	35.92	−0.71	25.0
160	0.1360	6.30	−13.53	−19.46	20.80	39.06	−1.64	25.2
200	0.2255	3.89	−10.64	−25.60	21.30	42.83	−2.86	25.0
240	0.351	2.64	−6.69	−33.42	22.50	47.30	−4.33	25.4
280	0.530	1.92	−2.91	−42.85	24.70	53.05	−6.34	25.6

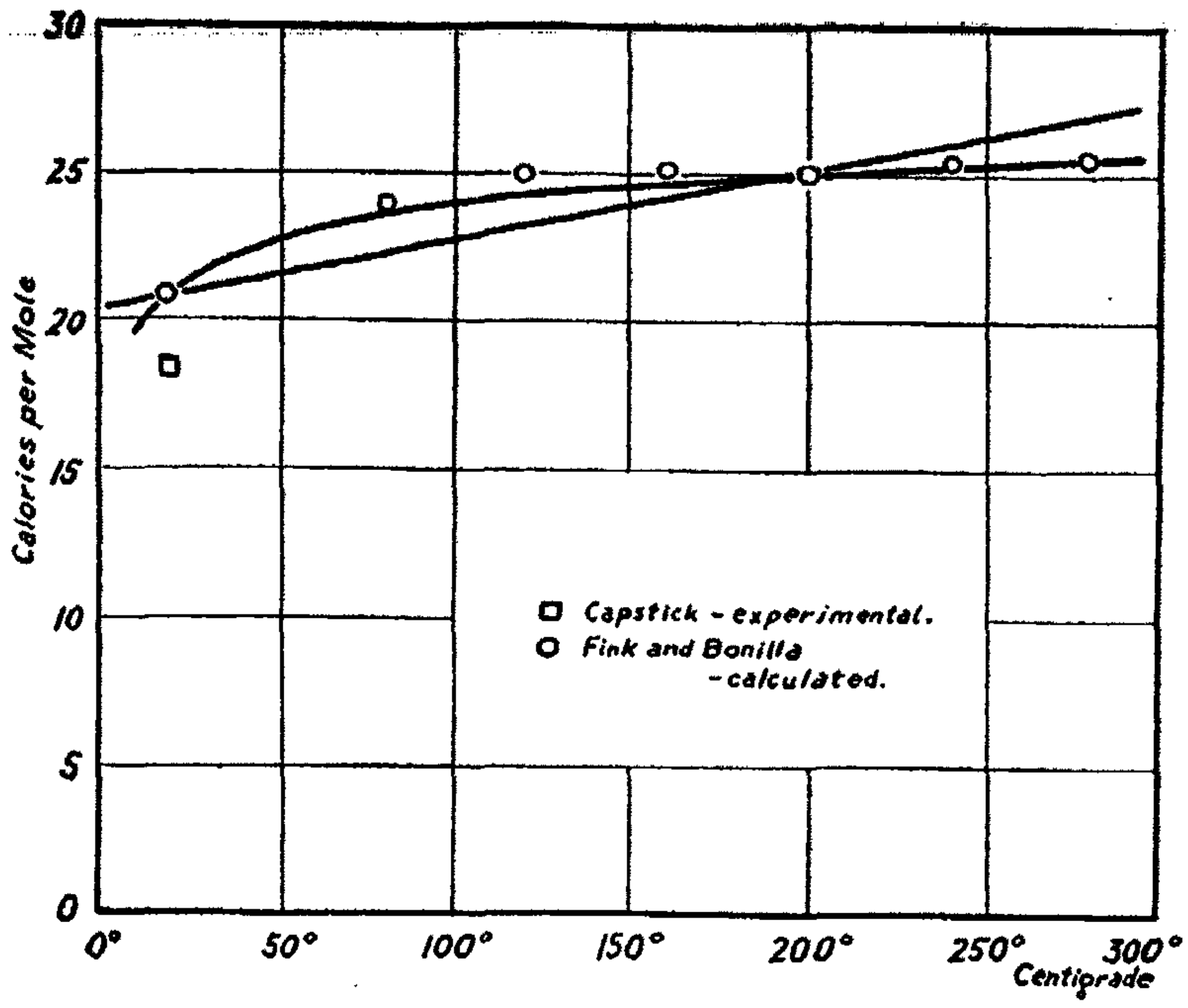

FIG. 1. C_p OF CARBON TETRACHLORIDE VAPOR AT 1 ATMOSPHERE

than 2 calories between 0°C. and 300°C. From the graph we find $C_{p,298}$ = 20.9.

If it is desired to fit an equation more closely to the calculated points, the following one may be used, which, plotted, gives the curve in figure 1, probably preferable for extrapolating:

$$C_p = 21.6 + 0.0073T - 1.4 \times 10^{35}\ T^{-10}$$

THERMODYNAMIC DATA FOR THE SUBSTANCES INVOLVED

C (graphite):
$C_p = -1.652 + 0.01676T - 0.00001727T^2 + 0.0^{8}994T^3 - 0.0^{11}263T^4$.
$C_{p,298} = 2.05$ calories per mole degree.
$S_{298} = 1.3$ calories per mole degree.
$C_p = 6.4 - 26{,}500/T^{3/2}$ (approximate, Fink and Bonilla).

$Cl_2(g)$:
$C_p = 7.4 + 0.001T$; $C_{p,298} = 7.7$.
$S_{298} = 26.62$ calories per atom degree.

CCl_4:
$\Delta H_{293}(g) = -25{,}430$ calories per mole.
$\Delta H_{298}(g) = -25{,}430 + 5(20.9 - 15.4 - 2.05) = -25{,}410$.
$S_{298}(l) = 49.06$.
$\Delta S_{298}(l)$ of $CCl_4 = 49.06 - 4 \times 26.62 - 1.3 = -58.72$.
ΔH_{298} (vaporization) $= 7{,}700$; $p_{298} = 114.7$ mm.
$\Delta H_{298}(l) = -25{,}410 - 7{,}700 = -33{,}110$.
$\Delta F^{\circ}_{298}(l) = -33{,}110 + 298 \times 58.72 = -15{,}610$.
$\Delta F^{\circ}_{298}(g) = -15{,}610 - RT(\ln 114.7 - \ln 760) = -14{,}490$ calories per mole at 1 atmosphere.
$C_p = 14.0 + 0.0233T$; $C_{p,298} = 20.9$.

$COCl_2$:
$\Delta H_{298}(g) = -51{,}920$; $\Delta F^{\circ}_{298}(g) = -48{,}960$ (8).
$p_{298} = 1500$ mm.
$\Delta F^{\circ}_{298}(l) = -48{,}960 - RT(\ln 760 - \ln 1500) = -49{,}370$.
$C_{p,298}(g) = 13.3$ (by interpolation; see later).

$CO_2(g)$ (9):
$\Delta H = -94{,}210 - 0.30T + 0.003T^2 - 0.0^{6}1T^3$; $\Delta H_{298} = -94{,}280$.
$\Delta F = -94{,}210 + 0.30\ T \ln T - 0.003T^2 + 0.0^{7}5T^3 - 0.94T$.
$\Delta F^{\circ}_{298} = -94{,}010$.
$C_p = 7.40 + 0.00667T - 0.0000015T^2$.

$SiCl_4$:
$\Delta H_{298}(g) = -142{,}650$; $\Delta H_{298}(l) = -149{,}100$.
$S_{298}(l) = 56.43$; $p_{298} = 234.5$ mm.
ΔS_{298} (formation) $= 56.43 - 4 \times 26.62 - 4.54 = -54.59$.
$\Delta F^{\circ}_{298}(l) = -149{,}100 + 298 \times 54.59 = -132{,}800$.
$\Delta F^{\circ}_{298}(\text{g, 1 atmosphere}) = -132{,}800 - RT \ln \frac{234.5}{760} = -132{,}100$.
$C_{p,298}(g) = 20.9$ (1 atmosphere; assumed equal to CCl_4).

$SnCl_4$:
$\Delta H_{298}(g) = -118{,}300$; $\Delta H_{298}(l) = -127{,}360$.
$S_{298}(l) = 61.84$; $p_{298} = 24.02$ mm.
$\Delta S_{298}(l)$ (formation) $= 61.84 - 4 \times 26.62 - 12.50 = -57.14$.
$\Delta F^{\circ}_{298}(l) = -127{,}360 + 57.14 \times 298 = -110{,}420$.
$\Delta F^{\circ}_{298}(g) = -110{,}420 - RT \ln \frac{24.02}{760} = -108{,}300$.
$C_{p,298}(\text{g, 1 atmosphere}) = 20.9$.

$AlCl_3$:

$\Delta H_{298}(s) = -167{,}000$; $\Delta H_{298}(g, 1\ \text{atmosphere}) = -140{,}620$ (10).

$S_{298}(s) = \frac{3}{2}R \ln 26.97 \times 35.455^3 - 3.76 = 37.97$ (see later).

$\Delta S_{298}(s)$ (formation) $= 37.97 - 3 \times 26.62 - 6.73 = -48.62$.

$\Delta F^\circ_{298}(s) = -167{,}000 + 298 \times 48.62 = -152{,}510$.

$p_{298} = 0.00025$ mm. (10); $C_p(s) = 6n = 24$ (assumed for 298).

$\Delta F^\circ_{298}(g, 1\ \text{atmosphere}) = -152{,}510 - RT \ln \frac{0.00025}{760} = -143{,}660$.

SiO_2 (quartz):

$\Delta H_{298} = -202{,}000$ (4, 11); $S_{298} = 9.81$ (see later).

$\Delta S_{298} = 9.81 - 4.54 - 2 \times 24.52 = -43.77$; $C_p = 10.7$.

$\Delta F^\circ_{298} = -202{,}000 + 298 \times 43.77 = -188{,}960$.

SnO_2 (amorphous):

$\Delta H_{298} = -137{,}800$; $\Delta F^\circ_{298} = -123{,}200$ (12); $C_p = 13.5$.

Al_2O_3 (amorphous):

$\Delta H_{298} = -384{,}000$ (11); $\Delta F^\circ_{298} = -356{,}600$; $C_p = 19.01$.

When not otherwise indicated, the source of data in this table is the International Critical Tables (4).

No data were found on the specific heat of phosgene gas. We will assume that the variation of C_p(g) along the series methane–methyl chloride–methylene chloride–chloroform–carbon tetrachloride should be quite similar to that for the series carbon dioxide–phosgene–carbon tetrachloride, as would be expected to be approximately true. Since, furthermore, the values of $C_{p,298}$ are almost equal for carbon dioxide and for methane, those for phosgene and for methylene chloride should similarly be equal. C_p for the latter compound, however, was not available in the literature, and has therefore been obtained by interpolation, in figure 2. The result is 13.3.

No data were found on S for aluminum chloride or any similar compounds, so Latimer's approximation was used, since aluminum has at 298°C. almost reached the Dulong and Petit value.

Although sufficient C_p data are available, the entropy of quartz has apparently not been calculated. This we have done graphically, using the well-known relationship:

$$S_T = \int_0^T \frac{C_p}{T}\, dT$$

The graphical integration gives 9.81 as the entropy of quartz at 298°C.

THE CHLORINATION OF C_2Cl_4 AND OF C_2Cl_6

One of the reactions of which the reverse is found to occur in several of the methods of decomposition of carbon tetrachloride is:

$$C_2Cl_4 + 2Cl_2 = 2CCl_4$$

Lob (13) has shown it to occur in the action of a hot platinum filament on carbon tetrachloride vapor. The only study of the thermal reaction has been that due to Weiser and Wightman (13), also on the decomposition of carbon tetrachloride, and very much from a practical point of view. Some fairly helpful results can be calculated from their data if the assumption is made that they approached the equilibrium, which seems likely. However, it must be remembered that this may not be the theoretical

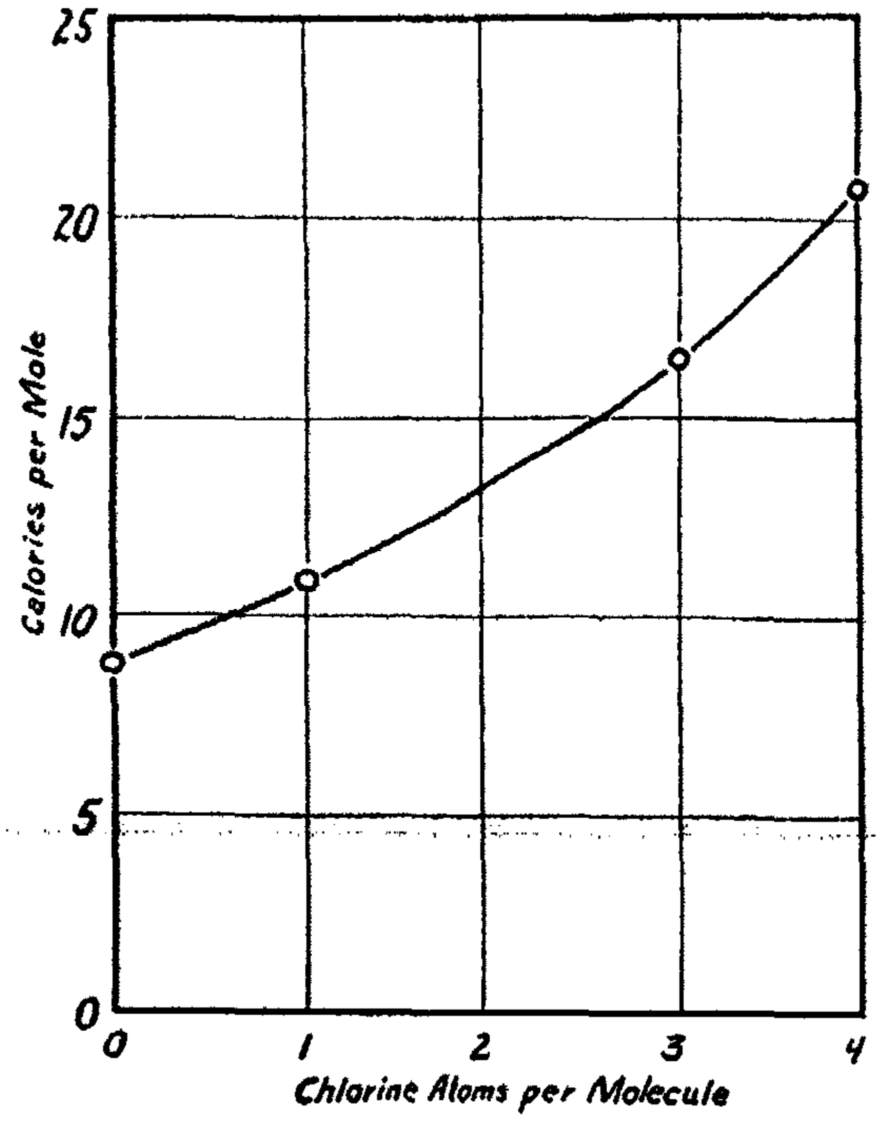

FIG. 2. C_p AT 298° K. AND 1 ATMOSPHERE FOR THE GASES CARBON DIOXIDE, METHANE, METHYL CHLORIDE, CHLOROFORM, AND CARBON TETRACHLORIDE

TABLE 2

The reaction $2CCl_4 = C_2Cl_4 + 2Cl_2$

(Calculated from Weiser and Wightman)

t (CORRECTED)	$1/T$	C_2Cl_4	CCl_4	Cl_2	TOTAL MOLES	TOTAL VOLUME	$\log_{10}K$	K_p	$\Delta F°$	ΔH
degrees C.		*moles*	*moles*	*moles*		*liters*				
750	0.000980	0.219	0.581	0.442	1.242	104	−2.91	0.00122	13,600	
850	0.000883	0.278	0.451	0.566	1.295	119	−2.42	0.00378	12,400	
900	0.000855	0.238	0.516	0.493	1.247	120	−2.74	0.00182	14,700	15,000
1025	0.000769	0.278	0.454	0.564	1.296	138	−2.51	0.00310	14,900	
1125	0.000714	0.351	0.297	0.572	1.220	140	−2.032	0.00928	13,000	

The number of moles given here is that obtained for a constant amount of carbon tetrachloride passed through the tube.

equilibrium; this will be discussed later. Weiser and Wightman's temperatures are for no gas flow, which we have approximately corrected to actual gas temperatures from data supplied by them. A further correction was made: the carbon tetrachloride unaccounted for was portioned up between CCl_4 and C_2Cl_4 in ratio of the two vapor pressures, using Duhring's rule. Table 2 shows our calculated results. The values for log K were plotted against $1/T$ in figure 3, and $\Delta H'$ obtained from the slope. The only check on these figures is given by Berthelot's incomplete heat of combustion data (14) from which we may say that ΔH of formation of $C_2Cl_4(g)$ will be greater than about $-40{,}000$ calories, so that ΔH for the decomposition of two moles of CCl_4 to C_2Cl_4 will be greater than 10,000 calories, compared with 15,000, the value from table 2. Therefore the chlorination of C_2Cl_4 to CCl_4 is thermodynamically quite possible, yet has never been accomplished empirically.

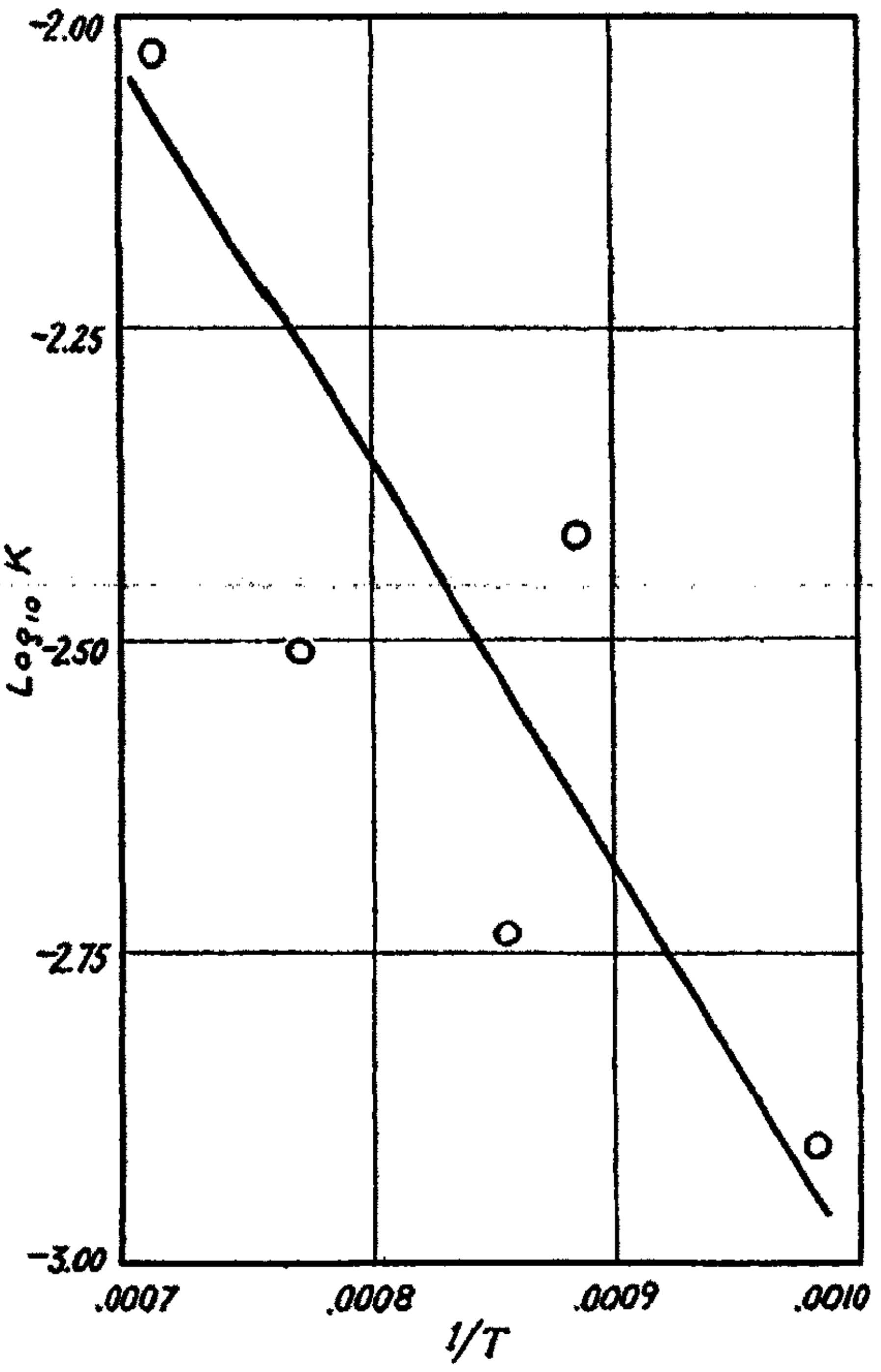

FIG. 3. EXTENT OF THE REACTION $C_2Cl_4 + 2Cl_2 \rightleftharpoons 2CCl_4$

Weiser and Wightman found the gas reaction,

$$C_2Cl_4 + Cl_2 = C_2Cl_6$$

to occur, but at a slower rate than the C_2Cl_4 formation between the temperature limits they used. At lower temperatures the velocity does not decrease as rapidly as may be expected, and it is appreciable at room temperature. Recently (15) the reaction in solution, as affected by light, has also been studied. Berthelot's figures on this reaction (16) are doubtless more accurate than his single heats of combustion, since the errors will cancel to some extent. His data give −54,000 calories for the heat absorbed at room temperature. From these two reactions we obtain the rough value of ΔH, 39,000 for

$$C_2Cl_6(g) + Cl_2 = 2CCl_4(g)$$

which is therefore endothermic, and favored by a temperature rise. This reaction, too, has never been directly carried out. The reverse action, however, has, and as early as 1839 Regnault (17) obtained C_2Cl_6 besides other substances in the following sequence with rising temperatures: C_2Cl_6, C_2Cl_4, C_2Cl_2, C_6Cl_6, C.

Except for carbon tetrachloride, the other carbon chlorides mentioned can all be produced consistently by the action of chlorine on carbon in a heated tube or in a carbon arc, as our own experiments and those of others have shown. Bolton (18), for instance, obtained C_2Cl_6 and C_6Cl_6 in an arc.

From these considerations it is seen that the splitting and chlorination of the inter-carbon bond in C_2Cl_4 and in C_2Cl_6 is the operation which has not been directly carried out so far. The problem seems to reduce itself to finding catalysts for these chlorinations, exothermic and endothermic, respectively, which will not simultaneously assist the decomposition to carbon and chlorine of the carbon tetrachloride formed.

Experimental

In an effort to duplicate Bolton's results and to determine simultaneously whether under any ordinary conditions carbon tetrachloride was produced, we constructed a Pyrex reaction chamber containing two axially perforated electrodes of carbon. The arc was run under varying conditions of length, current, and chlorine flow rate, and the gas was admitted through both carbons. Alternating current was used as well as direct. Another apparatus was constructed, containing a graphite rod heated electrically to the desired temperature in a stream of chlorine. In both of these setups mixtures of solid carbon chlorides, probably C_2Cl_6 and C_6Cl_6, were obtained on the walls and in the exit gas water condenser, but no carbon tetrachloride was obtained. Soaking the electrodes and rods in solutions of metal salts (copper, iron, and nickel) did not seem to make any difference. In the analysis for carbon tetrachloride the issuing gases were all completely condensed in a test tube by means of liquid air. This test tube was then transferred to a beaker containing an ice–salt mixture.

The gas boiling off came out through the tube previously used as inlet, which was of small bore, about 20 cm. long, and for this last operation it was thermally insulated from convection currents by means of a larger concentric tube. By regulating the amounts of salt and ice we found that the desired rate of heating up could be obtained. With this simplified column it was found possible to detect easily about 0.1 cc. of carbon tetrachloride in several cubic centimeters of liquid chlorine.

THE CHLORINATION OF PHOSGENE

A great deal of work has been done by others on the chlorination of metal oxides by chlorine, by phosgene, or by mixtures of carbon monoxide and chlorine, and by carbon and chlorine, on a laboratory scale, at least. All of the oxides tried have been successfully chlorinated, so that it is safe to assume, in general, that any metal chloride can be readily produced by means of cheap chlorinating agents. Silicon dioxide is the most refractory oxide, and when treated with chlorine only, the temperature must approximate 1000°C. before appreciable interaction sets in. It is the only common oxide or anhydride that cannot be chlorinated by phosgene below 600°C.

Chlorinations can also be readily carried out by means of carbon tetrachloride vapor (19, 20), and we felt that some of these latter reactions might be reversed under attainable conditions, particularly the reaction involving silicon dioxide. Three of these reactions were studied by us, experimentally and theoretically. The free energy changes calculated for the reactions show why chlorination by carbon tetrachloride is so successful.

Pyrex glass bomb tubes were dried by heating overnight to more than 600°C. with a slow stream of carbon dioxide dried over magnesium perchlorate, $Mg(ClO_4)_2$, passing continually through the bombs. We then placed the bombs in an ice–salt freezing mixture and passed in and condensed the phosgene and added the metal chloride by means of a special funnel to prevent wetting the stem. Otherwise good seals were difficult. The bombs were then heated for a day at a time to successively higher temperatures. Before raising the temperature each time, the bombs were cooled and inspected for the production of any solid oxides. The following reactions were studied:

Reaction I

$$2COCl_2(g) + SiCl_4(g) = 2CCl_4(g) + SiO_2$$

Approximately a dozen bombs were prepared with up to 4 cc. of each reactant as a liquid, in a total volume of 12 to 15 cc. Several were exposed for days to sunlight, others to a mercury vapor arc, and all were heated to temperatures ranging up to 540°C. Two withstood this temperature and the large pressure involved without bursting. Traces of other chlorides, ferric chloride and aluminum chloride, had been added to two of the bombs to test for any catalytic action. In practically none of these tubes was there found any silicon dioxide deposited on the walls, or any other indication of reaction. Under the mercury arc a rather dense cloud always formed which would later disappear in a few hours or a day, even with the bomb at below 0°C. Quickly breaking the bomb after an exposure to the arc left only the merest amount of powder after the evaporation of the liquids. No corrosion of the glass by the phosgene was noticed, though some investigators (21) have been troubled by such an action on other types of glass.

Reactions II and III

$$3COCl_2(g) + 2AlCl_3(g) = 3CCl_4(g) + Al_2O_3$$
$$2COCl_2(g) + SnCl_4(g) = 2CCl_4(g) + SnO_2$$

Two bombs with aluminum chloride and two with stannic chloride were prepared and treated similarly to those with silicon tetrachloride. Aluminum chloride was used because of its ready availability and stannic chloride because of its similarity to carbon tetrachloride. None of these bombs showed the formation of any oxide, which could have formed according to the above reactions. Even with C_2Cl_6 as an end product no oxides were formed; this reaction should have a greater tendency to occur, as we have already indicated.

Free energy calculations suggest the non-occurrence of the reactions to be due to lack of tendency toward the change rather than to lack of a catalyst. Calculations for 25°C. give the following results:

Reaction I (SiO_2): $\Delta F^\circ = +12{,}080$; $\Delta H = -6{,}370$; $\Delta C_p = +9.6$
Reaction II (Al_2O_3): $\Delta F^\circ = +43{,}000$; $\Delta H = +3{,}100$; $\Delta C_p = +7.8$
Reaction III (SnO_2): $\Delta F^\circ = +56{,}100$; $\Delta H = +33{,}500$; $\Delta C_p = +5.0$

Because of the magnitude of the free energy change, reactions II and III are seen to be hopeless, but reaction I merits a little study. If the three chlorine-containing compounds are in their liquid forms, ΔF° becomes +11,360. The effect of increases in temperature and pressure were approximately calculated, assuming ΔC_p to remain constant over the range.

$$\left(\frac{dF}{dT}\right)_p = -S = -\int \frac{C_p}{T}\,dT = -C_p \ln T + A$$

$$\Delta F_{T_2} - \Delta F_{T_1} = -\int_{T_1}^{T_2} (C_p \ln T + A)\,dT = \left(-C_p T \ln T + (1 - A)T\right)\Big]_{T_1}^{T_2}$$

ΔF° can be calculated closely enough for our purposes by knowing ΔH and assuming ΔC_p constant down to absolute zero. Knowing now ΔF° at two different temperatures, the value of $(1 - A)$, Lewis and Randall's I, can be calculated and

$$\Delta F^\circ_T = -7860 - 5\,T \ln T + 95.1T$$

Thus ΔF° rapidly increases with temperature, decreasing the reaction tendency. For a pressure change

$$\Delta F_{p_a} = \Delta F^\circ_1 - RT \ln \frac{a^2_{\mathrm{CCl_4}}}{a^2_{\mathrm{COCl_2}}\, x\, a_{\mathrm{SiCl_4}}}$$

where, approximately,

$$RT \ln a = \int_1^p V \mathrm{d}p$$

for each substance. There is practically nothing in the literature on the gaseous molar volumes (or densities) of the substances involved, so only a rough calculation assuming $a = p$, or, in general, that the activity coefficients cancel, can be carried out. For the greatest yield with a given total pressure P of phosgene and silicon tetrachloride, the pressure of phosgene should be $2P/3$, as can be shown by setting

$$M = p^2_{\mathrm{COCl_2}}\, x\, p_{\mathrm{SiCl_4}};\ p_{\mathrm{COCl_2}} + p_{\mathrm{SiCl_4}} = P$$

and making $\mathrm{d}M/\mathrm{d}p_{\mathrm{COCl_2}}$ equal to zero. A final pressure of carbon tetrachloride of 1 atmosphere will be assumed, which in the bombs would have amounted to a deposit of silicon dioxide of about 25 mg. Therefore at a given temperature

$$\Delta F = RT \ln \tfrac{1}{4} p^3_{\mathrm{COCl_2}}$$

and at 230°C., just above the critical temperatures of the substances involved, $p_{\mathrm{COCl_2}}$ amounts to 3700 atmospheres. The pressure actually would exceed this value, as can be seen from Dodge's reduced pressure versus compressibility curves (22). For the reaction between the liquids rather than the gases, and at 25°C., p is obtained as 740 atmospheres, so that if the reaction velocity is appreciable it would not be impossible to carry out the reaction under these conditions, but probably not commercially in spite of the small work of compression of the liquids.

The effect of the ultra-violet light from the mercury vapor arc lamp was obviously not merely catalytic, as the reaction reversed on removal of the light source, but the light also shifted the equilibrium. This is therefore another action that might be utilized.

THE DIRECT CHLORINATION OF CARBON

Our previously mentioned attempts to carry out the direct chlorination of carbon by chlorine to form carbon tetrachloride indicated that a catalyst was necessary. The reaction is decidedly exothermic and $\Delta F°$ of formation under standard conditions of gaseous carbon tetrachloride at 25°C. is −14,500.

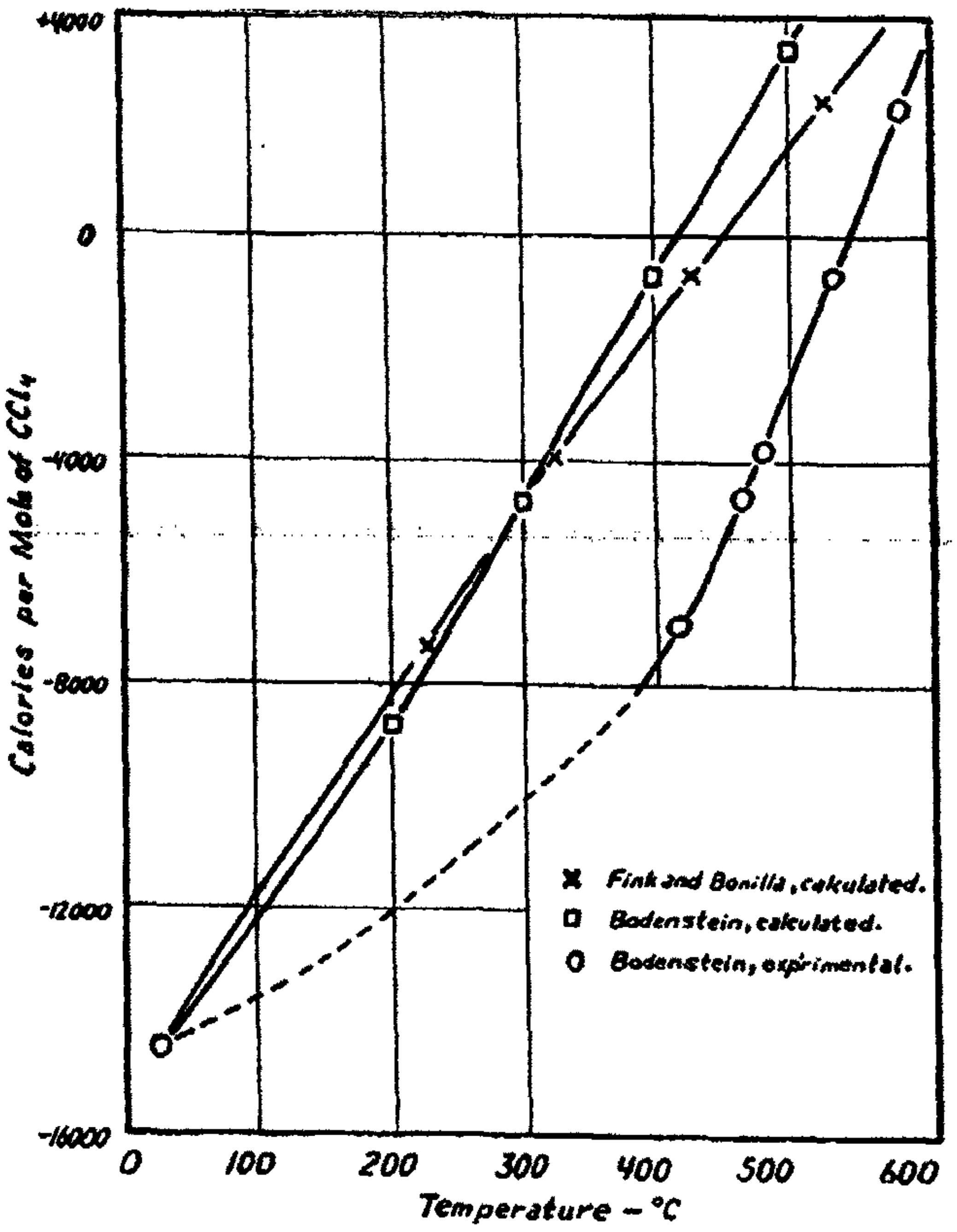

FIG. 4. EXTENT OF THE REACTION $CCl_4 \rightleftharpoons C + 2Cl_2$

After many fruitless attempts to find a catalyst, it was decided to attempt to reach equilibrium from the carbon tetrachloride side of the reaction:

$$C + 2Cl_2 = CCl_4$$

At this time Bodenstein's (23) work along this line appeared. His results are plotted in figure 4. They show that it is probably necessary to work at a temperature not over about 500°C. in order to synthesize carbon tetrachloride. Needless to say, this equilibrium was reached by Bodenstein from only one side, and is not very near the thermodynamic or calculated equilibrium. The values for the curves, calculated from Bodenstein's data, are given in table 3. The Nernst heat theorem values (24) have also been plotted, though they involve the rough "chemical constants." We find by using the simpler relationship for C_p(g) of carbon tetrachloride already obtained, and for carbon, the simpler of the expressions given:

$$\Delta H_T = \Delta H_0 + \Delta C_p dT = 21{,}160 + 7.2T - 0.01065T^2 + \frac{53{,}000}{T^{1/2}}$$

TABLE 3

Extent of the reaction $CCl_4 = C + 2Cl_2$

(Calculated from Bodenstein's results)

TEMPERATURE	CARBON TETRACHLORIDE DECOMPOSITION	$-\log_{10}K_p$	CHLORINE FRACTIONAL PRESSURE	$\Delta F°$
degrees C.	*per cent*			*calories per mole*
298	—	—	—	14490
417	4.06	2.18	0.078	6900
462	10.0	1.38	0.182	4650
477	13.9	1.10	0.244	3780
530	36.5	0.20	0.535	735
580	66.7	−0.506	0.800	−1790

on substituting the known value of ΔH_{298}. Since $\Delta F°_{298}$ is also known, the general free energy expression is obtained:

$$\Delta F^\circ_T = 21{,}160 - 16.6T \log T + 0.01065T^2 + \frac{35{,}300}{T^{1/2}} + 8.66T$$

These signs of ΔH and ΔF are for the decomposition of carbon tetrachloride. Values of equilibrium partial pressure of chlorine for 1 atmosphere total pressure were plotted in figure 5. The results of the calculations are shown in table 4. The agreement with the rough heat theorem values is seen from the curve to be fairly close.

Stock (24) has recently succeeded in producing some carbon tetrachloride by the action of chlorine on activated charcoal between 400°C. and 600°C. at pressures between 1 and 4 atmospheres. His results were not very reproducible, but interesting. The maximum pressure of carbon tetrachloride that he obtained was at 400°C. and 4.1 atmospheres total pressure, and amounted to 0.29 atmosphere, certainly quite sizeable. Assuming the gas pressure quotient to hold constant over the pressure range, we can

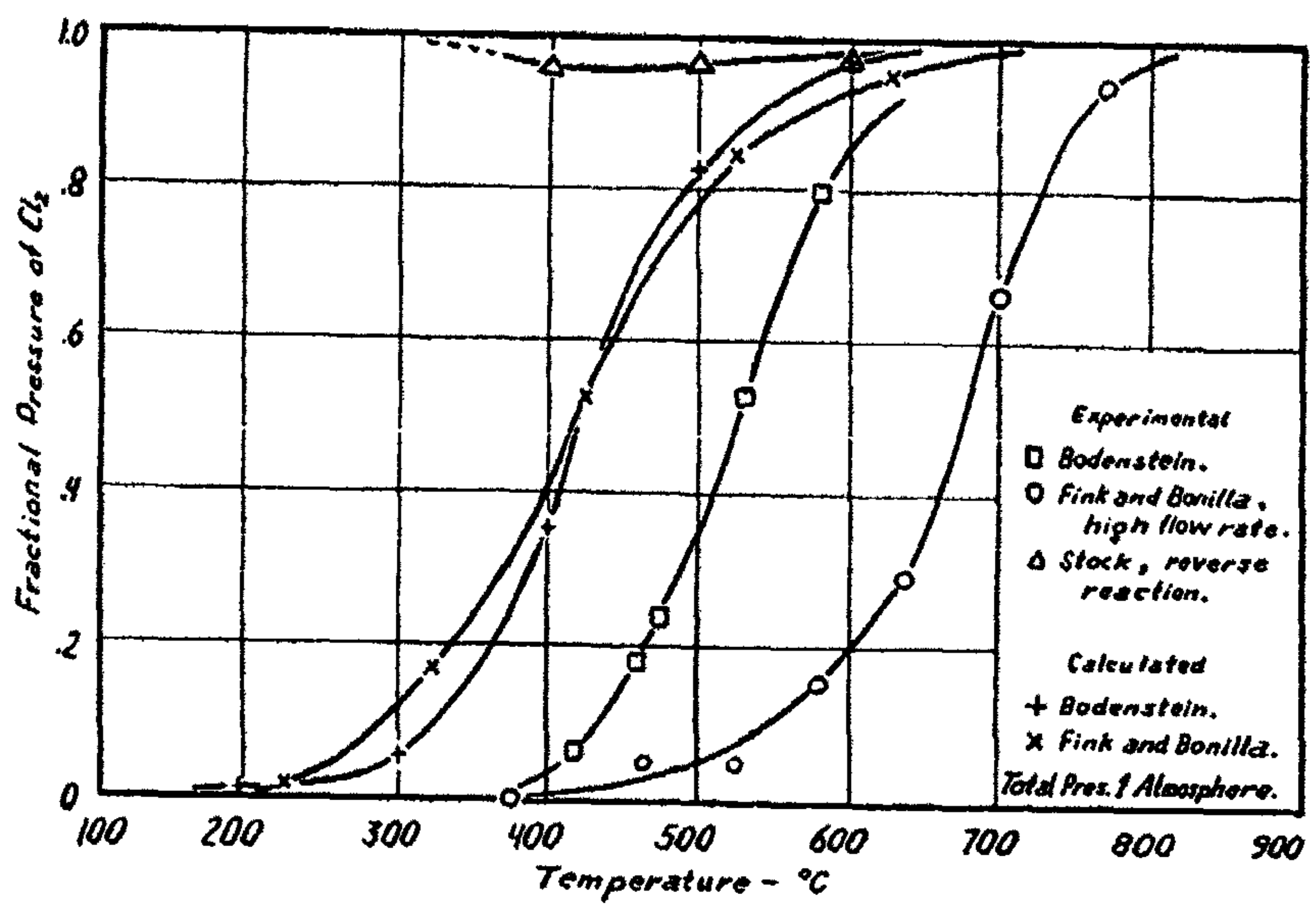

FIG. 5. FREE ENERGY CHANGE OF THE REACTION $C + 2Cl_2 \rightleftharpoons CCl_4$

TABLE 4

Theoretical extent of the reaction $CCl_4 = C + 2Cl_2$

TEMPERATURE	$\Delta F°$	$-\log_{10}K_p$	K_p	CHLORINE FRACTIONAL PRESSURE
Absolute	*calories per mole*			
500	7342	3.20	0.00063	0.0248
600	3955	1.437	0.0364	0.1735
700	725	0.226	0.594	0.529
800	−2426	0.661	4.58	0.846
900	−5359	−1.300	19.95	0.954

TABLE 5

The reaction $C + 2Cl_2 = CCl_4$

(Calculated from Stock's experiments)

TEMPERATURE	TOTAL BOMB PRESSURE	PARTIAL CHLORINE PRESSURE	PARTIAL CARBON TETRACHLORIDE PRESSURE	PRESSURE QUOTIENT K_p	PARTIAL CARBON TETRACHLORIDE PRESSURE AT 1 ATMOSPHERE TOTAL PRESSURE
degrees C.	*atmospheres*	*atmospheres*	*atmospheres*		*atmospheres*
400	2.5	2.12	0.204	0.0453	0.0416
500	1.65	1.56	0.088	0.0365	0.034
600	1.65	1.58	0.065	0.027	0.0256

calculate that the partial pressure of carbon tetrachloride will equal that of chlorine at a total pressure of about 40 atmospheres. Stock's maximum yields of carbon tetrachloride do seem to indicate a limit of reaction. We have made the appropriate calculations from them, and give the results in table 5. These values we have also plotted in figure 5, and the combination of theoretical and experimental curves for the equilibrium is strikingly similar to the curves given by Duhem (2).

Experimental

We decided to use the decomposition reaction to find a catalyst for the reaction of synthesis, knowing that the same catalyst should theoretically catalyze both opposing reactions. An apparatus was set up in which carbon tetrachloride vapor was produced by boiling the liquid in a graduated flask. The vapor passed through a Pyrex combustion tube in an electric heater. The tube contained a thermocouple hot junction, and in it were placed in different runs the various materials to be tested for catalytic effect. The gases next traversed a gas sampling tube maintained at about 80°C. to prevent condensation of the carbon tetrachloride, and from there were removed by a water jet suction pump in which the pressure was regulated by an air admission valve. A run was ended when the conditions of temperature and flow rate had remained constant for about 30 minutes, which corresponds to a large volume of carbon tetrachloride vapor, as the average flow rate was about 2 cc. of liquid carbon tetrachloride per minute. An excess of strong potassium iodide solution was admitted to the sampling tube, the liquid shaken about, poured out, the tube rinsed with alcohol, and solution and rinsings titrated with standard sodium thiosulfate solution and starch indicator, for free iodine. The partial pressure of chlorine was calculated, knowing the volume of the sampling tube (300 cc.) and the temperature at which it had been held. The carbon tetrachloride pressure was obtained by difference, for which purpose a manometer was connected to the system.

In order to obtain correct results with the above scheme it is necessary that chlorine and carbon should be the only decomposition products of the carbon tetrachloride. With some of the substances tested as catalysts solid and liquid products such as C_2Cl_6, C_2Cl_4, C_6Cl_6, etc., were produced in varying quantities. Many wood charcoals and silicon dioxide were among this class of substances. Ordinary granulated animal charcoal of 88 per cent ash was the best catalyst for the total decomposition, even when present in only small amounts, and no liquid or solid products of carbon tetrachloride decomposition ever condensed when the animal charcoal was used. Runs were made between 300°C. and 800°C. The results have been plotted alongside Bodenstein's curve in figure 4. The total time that the carbon tetrachloride vapor remained in the heated portion of the tube we calculate to have been about 2 seconds, excluding the adsorption by the charcoal. Furthermore, at this high flow rate it is probable that the vapor did not reach the temperature indicated, as the charcoal was never packed tightly and the granules were coarse. The animal charcoal was therefore a very effective catalyst for this reaction, and undoubtedly more active than the charcoal Bodenstein used, though it is difficult to determine how much his reaction rates were affected by diffusion velocity. When chlorine was passed through the heated tube at various temperatures and rates, there was, however, no noticeable carbon tetrachloride formation, using the same system of freezing and redistilling the outcoming gases as previously described under the C_2Cl_4 and C_2Cl_6 reactions.

Since pressure aids the formation of carbon tetrachloride by direct synthesis, according to Le Chatelier's principle, an iron bomb was prepared and filled with a mixture of several brands of active charcoals, including the animal charcoal already used. Liquid chlorine was condensed in the bomb, which was then closed and heated for 60 hours in a sand bath at approximately 170°C. Upon opening, a mixture of solid and liquid chlorides of carbon was found, as well as iron and lead chlorides (the latter from the lead gaskets), but no carbon tetrachloride could be detected.

Thus it is seen that the direct chlorination of carbon by chlorine to form carbon tetrachloride is a reaction that is quite particular as to its catalyst. Stock seems to have struck a charcoal that serves the purpose, though apparently not specially well, but none of the substances we have tested seem to have any value along this line, including a very porous graphite prepared at 4000°C.

It is not impossible, of course, to explain by the catalyst poisoning theory why these two reactions should not reach the calculated equilibrium. It is merely necessary to assume that Bodenstein's catalyst was poisoned by the chlorine which was formed, but not by carbon tetrachloride, whereas Stock's catalyst was affected in exactly the reverse manner. More work along this line will undoubtedly clear up the situation, and show whether some simple assumption is correct, or whether there are complications or an entirely different phenomenon.

THE REACTION $2COCl_2 = CCl_4 + CO_2$

From the thermodynamic data already given, we find for the above reaction $\Delta F^\circ_{298} = -9580$ calories and $\Delta H_{298} = -15,870$ calories. Therefore, there is a decreasing tendency for the left-to-right reaction at higher temperatures, assuming ΔC_p to remain small. At about 500°C., however, the carbon tetrachloride equilibrium pressure ought yet to be appreciable and readily determinable, as well as that of carbon dioxide. Stock and Wustrow (25) have calculated several points on the theoretical equilibrium curve, by the use of the heat theorem. We have calculated the position of the equilibrium over a broader band of temperatures, using the thermodynamic data we give above. We have assumed that phosgene has a value of C_p which approximates the average of the values for carbon dioxide and carbon tetrachloride. Therefore ΔC_p will remain small, and will be assumed constant at +3.2, the figure based on our data for 25°C. These data yield:

$$\Delta F^\circ = -16{,}824 - 7.375T \log T + 42.5T$$

Starting with this equation, the values for ΔF°, $\log K$, and fractional phosgene pressure have been calculated and are given in table 6.

The formation of phosgene from carbon monoxide and chlorine has been thoroughly studied and commercial-sized plants built for its manufacture (26). Therefore phosgene could undoubtedly be a practical source of carbon tetrachloride, or rather, simply an intermediate product, if a suitable catalyst were found. Quantitative studies of reactions involving phosgene have been made frequently, and for widely varying conditions (27, 28). But seldom have other reactions than $COCl_2 = CO + Cl_2$ and its intermediate steps been investigated, and no carbon tetrachloride has apparently ever appeared when its presence was not desired, or expected. The formation of carbon tetrachloride from phosgene has been reported only by Stock (21, 25), and in very small amounts. The static method he used does not lend itself to accurate results, owing to the small volumes of carbon tetrachloride produced, although it has an important advantage in permitting of long reaction periods. Accordingly, we investigated the decomposition of phosgene by the dynamic method. We decided to attempt to carry out the reaction at as low temperatures as possible, by the use of suitable catalysts if they could be found, to eliminate the multiplicity of other reaction products than carbon dioxide and carbon tetrachloride, such as carbon monoxide, chlorine, hexachloroethane, etc., which complicate the analysis and the interpretation of results.

TABLE 6

Calculated equilibrium for the reaction $2COCl_2 = CCl_4 + CO_2$

TEMPERATURE	$1/T$	ΔF°	$-\log_{10} K_p$	PHOSGENE FRACTIONAL PRESSURE
degrees C.	*Absolute*	*calories*		
162	0.0023	−6784	−3.41	0.019
203	0.0021	−5984	−2.745	0.041
267	0.00185	−4754	−1.92	0.098
352	0.0016	−3144	−1.10	0.220
496	0.0013	−494	−0.140	0.460

Starting with pure phosgene, the reaction products to be expected at the low temperatures at which carbon tetrachloride will not decompose are carbon dioxide and carbon tetrachloride in equal concentrations and carbon monoxide and chlorine, the formation of which is to be minimized, also in equal concentrations. From the methods mentioned by Olsen (29) for the determination of phosgene, we found the precipitation with aniline most convenient. Chlorine was first removed by means of antimony trisulfide, then phosgene and carbon dioxide by a water solution saturated with aniline and about half saturated with strontium hydroxide. We found that under these conditions phosgene did not hydrolyze and precipitate any strontium carbonate, to interfere with the carbon dioxide determination. Also, the diphenylurea precipitate obtained by the action of phosgene on the aniline was not soluble in the strontium hydroxide solution, though it does dissolve in stronger alkaline solutions. The carbon monoxide and carbon tetrachloride present in the gas mixture were not determined directly. In the apparatus used, phosgene as a gas leaves a cylinder through a needle valve. The rate is measured by a flowmeter containing sulfuric acid, a correction for pressure being applied, for accurate results, from the reading of a special manometer. The phosgene then passes through the reaction tube which contains any catalyst being tested, and is heated electrically. A three-way cock permits the issuing gases to follow a by-pass and be finally exhausted by a water jet suction pump. When the conditions have remained constant a sufficient time, depending on the flow rate and on the age of the catalyst, the cock is turned to permit the gases to enter the absorption train. Liebig bulbs contain the antimony trisulfide and a bubble bottle holds the aniline–strontium hydroxide solution. By regulating line and air admission cocks the pressure in the system can be maintained at slightly above atmospheric. This is to prevent, practically, the entrance of air, which would oxidize phosgene to carbon dioxide, besides introducing a small amount of carbon dioxide otherwise. Perfectly dry antimony trisulfide, the chlorine absorbent, never absorbed any phosgene, nor gave other trouble. The aniline–strontium hydroxide solution was kept and handled entirely like a standard caustic solution, and never touched the air after being prepared. It was kept in a dark bottle to prevent discoloration. In preparing the absorption train flask the train was first filled with pure nitrogen, then the solution admitted. After a run the solution and precipitates were blown back by nitrogen through the gas inlet tube and into a Gooch crucible fitted with an air-tight stopper. After thorough washing with water the crucible was dried to constant weight at 75°C.—24 hours in an electric oven was sufficient—and weighed. The diphenylurea was then leached out by alcohol in a Soxhlet extractor. The crucible was again washed with water and dried at 75°C., the difference in weight being taken as diphenylurea. Now the strontium carbonate was leached out with dilute hydrochloric acid and the crucible washed and dried as before, giving strontium carbonate by difference. The weight of chlorine absorbed was given directly by the gain in weight of the antimony trisulfide tube, as the displaced sulfur remains in the tube. The phosgene used contained some carbon monoxide as impurity. No carbon dioxide and merely the slightest trace of chlorine were found in it, by a blank run. The excess pressure of the cylinder over that of pure phosgene was approximately 5 per cent at the beginning and decreased as more of the gas was used. No hydrogen chloride was found in the phosgene, no test for hydrogen sulfide being obtained after passing over antimony trisulfide.

Experimental

With this apparatus numerous runs were made at 500°C. with the heating tube empty and with different varieties of carbon in it. Animal charcoal gave a substantial decomposition to chlorine and carbon monoxide and gave no carbon dioxide, so it was not used again. Wood charcoals gave little, if any, chlorine, but also practically no carbon dioxide. A very adsorbent and highly activated variety of alkaline black ash charcoal was used in many runs, both alone, and impregnated with solutions of metal salts and then outgassed at a high temperature. Nickel sulfate, copper sulfate, cobalt sulfate, ferric sulfate, and chromium sulfate were used. All of the runs gave the same result, no carbon dioxide, nor, presumably, any carbon tetrachloride. The weights of strontium carbonate obtained averaged about 1.0 mg., and decreased as experimental technique improved. These small weights were probably due to slight infiltration of air. In these runs very little decomposition of the phosgene to carbon monoxide and chlorine occurred, on account of the reaction's sensitivity for a catalyst. Flow rates were as small as 2 cc. per minute, and the heated volume of the tube about 25 cc. The aniline–strontium hydroxide solution was saturated with strontium carbonate, as carbon dioxide-free water was not used in its preparation. All washings were, however, with distilled and recently boiled water, to minimize the solubility of the carbonate.

For its possible interest, a previously used method of analysis will be mentioned, which was perfectly satisfactory for this gas mixture, but is not very sensitive. The issuing gases were passed through gas sampling tubes until at least ten volumes had passed, and then were treated quickly with strong sodium hydroxide solution in a Hempel pipette and gas burette. Simultaneously, a volume of nitrogen was admitted, sufficient to retain the carbon tetrachloride present in the gaseous state. The remaining nitrogen, carbon tetrachloride, and carbon monoxide were passed into another pipette containing some thin paraffin oil saturated with air, and the carbon tetrachloride dissolved quantitatively. The carbon monoxide is lastly determined as usual by means of cuprous chloride. Thus we have determined the volumes of carbon monoxide, of carbon tetrachloride, and of the total gas mixture (that of the sampling tube), sufficient data to calculate the pressure quotient. Phosgene, obtained by difference, constitutes ordinarily the largest part of the total volume, so that little error is introduced in that way. If the gases after the caustic treatment are to be retained over a liquid, mercury should be used, as carbon tetrachloride vapor assumed at 1 atmosphere and 25°C. is soluble in about eight times its volume of water. This method, besides being very rapid, has the advantage that the carbon tetrachloride can be directly recovered afterward.

TABLE 7

Gas absorption by light paraffin oil, at room temperature

RUN NO.	CONDITION OF AIR	CONDITION OF OIL	INITIAL VOLUME	FINAL VOLUME	CALCULATED FINAL VOLUME
			cc.	cc.	cc.
1	Pure, dry	Saturated with air	88.0	88.0	—
2	Pure, dry	Free of air	92.15	92.1	—
3	Saturated with water	Saturated with air	64.6	64.6	—
4	About 50 per cent carbon monoxide	Saturated with air	24.1	24.1	—
5	Saturated with water and carbon tetrachloride	Saturated with air	88.8	76.0	75.95
6	Saturated with water and carbon tetrachloride	That used in No. 5	96.9	82.9	82.88

The oil we used was a standard light paraffin lubricating oil of the following physical properties: density at 27°C., 0.877; flash point, 196°C. (385°F.); fire point, 229°C. (445°F.), both by the Cleveland open cup tester. We found that 15 minutes of gas–oil contact time with frequent shaking was sufficient for equilibrium. In table 7 are given our tests to establish the utility of the method. Run 1 shows that the oil has no appreciable vapor pressure at room temperature; runs 2, 3 and 4 that air, water, and carbon monoxide are practically insoluble in it; and runs 5 and 6 that carbon tetrachloride vapor in small quantities is practically completely dissolved from air. Stock has already shown that concentrated potassium hydroxide solution can effectively dissolve phosgene and carbon dioxide without hydrolyzing carbon tetrachloride appreciably, nor dissolving it.

THE REACTION $CO_2 + CCl_4 = 2COCl_2$

The reverse reaction of the one just discussed, or the formation of phosgene from carbon dioxide and carbon tetrachloride, was next taken up, to attempt to reach the equilibrium experimentally from that side, and to improve on the few and rather unreproducible data of Stock (21).

The apparatus we constructed is shown in figure 6. Carbon dioxide evaporates in the cylinder A and escapes through a needle valve into the system. The flow rate is measured by the oil-filled flowmeter B. The manometer C gives the gage pressure within the saturator D, which contains carbon tetrachloride and is surrounded by a water bath (F) to increase the heat capacity and minimize temperature fluctuations. When lower than room temperatures are desired, running water is employed to cool the saturator. Its temperature is given by the thermometer E. The gases then pass through a bubble bottle containing anhydrous magnesium perchlorate. Next they enter the reaction tube H, which is heated by the electric heater J. A fused nitrate bath is contained in the iron pot I. The issuing gases fill and traverse the gas sampling tubes L and L′, and the issuing phosgene is destroyed by a water jet suction pump.

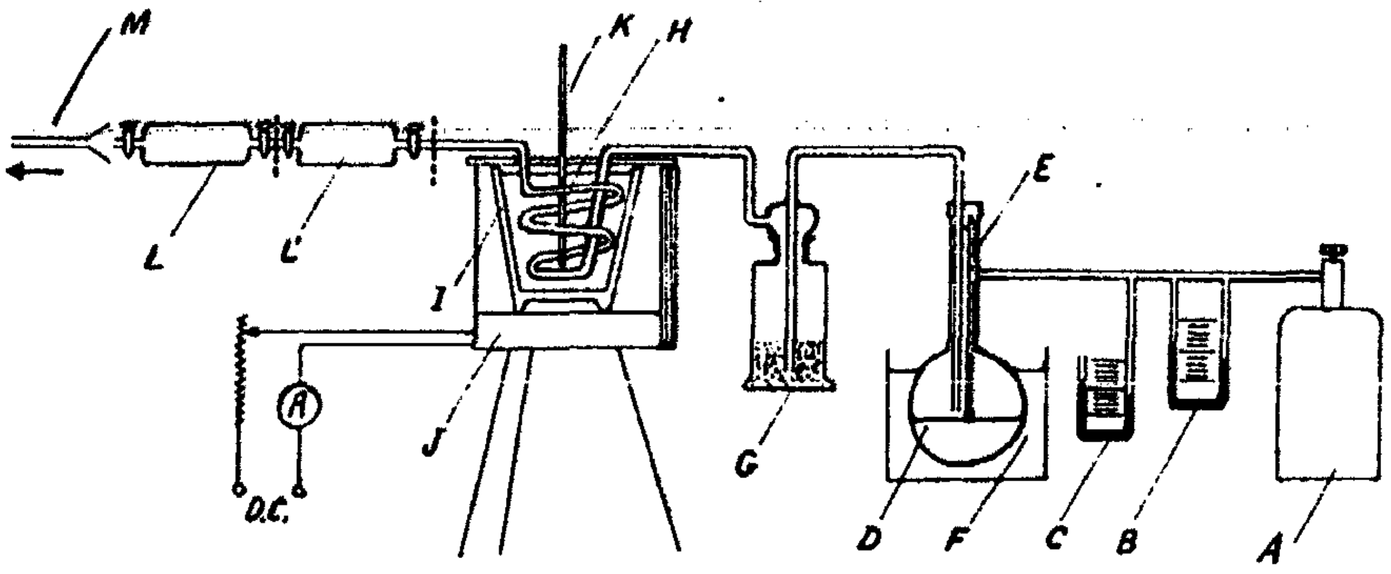

FIG. 6. SET-UP FOR THE FORMATION OF PHOSGENE

The carbon dioxide practically saturated itself with carbon tetrachloride. This can be shown to be true by a brief calculation, knowing a figure for evaporation rate of carbon tetrachloride. The variables will be:

p' = carbon tetrachloride saturation pressure, in atmospheres.
p = actual carbon tetrachloride pressure, in atmospheres.
P = pressure of carbon tetrachloride and carbon dioxide, in atmospheres.
K = rate of evaporation of carbon tetrachloride, in moles per second $\times$ cm^2.
A = Effective liquid area, in cm^2.
Q = moles per second carbon dioxide flow.
$(p'-p)/p' = S$ = fraction of unsaturation.

The result is:

$$\ln S = \frac{-KA(P-p)}{Qp'}$$

Using $K = 6 \times 10^{-6}$, calculated from available data (30), we get $\ln S = -6.2$, or S is 0.2 per cent for our average conditions. As the temperature changes, K and p' should vary somewhat similarly, so that this value of S should hold over the range of room temperatures.

The pressure p' was calculated from the relationship

$$\log p' = 7.8717 - 1732/T$$

which we obtained by plotting data for p' of carbon tetrachloride between 0°C. and 50°C. (4, 30). The best curve through the points plotted as log p' against $1/T$ is this straight line, and the deviations are quite small. This equation gives the pressure of the liquid in contact with only the pure vapor. Owing to the added carbon dioxide pressure, the change in carbon tetrachloride vapor pressure is given by:

$$(\mathrm{d}p'/\mathrm{d}P)_T = V_l/v_g$$

At 30°C. $\mathrm{d}p'/\mathrm{d}P$ thus amounts to 0.00065, and Dp' is 0.33 per cent of p'. This error is in the opposite direction from that previously calculated for lack of saturation of the carbon dioxide with carbon tetrachloride, and both will be neglected. At the low pressures of 1/6 atmosphere it was assumed that carbon tetrachloride vapor obeys the gas laws closely enough in these calculations.

In the apparatus, the Pyrex helix had a heated volume of 75 cc., and the bath was a eutectic mixture of sodium nitrate and potassium nitrate. This method of heating gives much greater uniformity of temperature than is obtained in a tube in an ordinary electric heater. One side of the pot we thermally insulated better than the other, so that a gentle convection current was obtained. The gases were dried by magnesium perchlorate to prevent carbon tetrachloride hydrolysis and hydrogen chloride formation, which would be included as phosgene in the analytical method finally adopted.

Since the gas mixture after reaction will be entirely composed of carbon tetrachloride, carbon dioxide, and phosgene if there is no chlorine present, only two data are necessary for the analysis, besides this fact. We decided that greatest accuracy would be attained by using: (a) the ratio of moles of phosgene to carbon dioxide in the gases after the reaction, and (b) the ratio of moles of carbon tetrachloride to carbon dioxide before the reaction. (a) can be determined by the usual analytical methods, and (b) from the saturator temperature and pressure. Thus, starting with gas sampling tubes filled with nitrogen it is not necessary to displace the foreign gas completely before the correct result can be obtained. In the chemical analysis standardized solutions of sodium hydroxide, sulfuric acid, and silver nitrate were used. For 50 cc. of the caustic solution the sulfuric acid titre to the phenolphthalein end point was known. After a run, that volume of the caustic was admitted to the sampling tube by a pipette, the tube shaken thoroughly, but not long enough to hydrolyze carbon tetrachloride, and the solution and rinsings were titrated to the same phenolphthalein end point. The decrease in cubic centimeters of sulfuric acid solution required, calculated to moles of the acid, is equal to 1/2 the number of moles of carbon dioxide absorbed plus 3/2 the number of phosgene moles absorbed. The solution was then made to the correct acidity and the moles of phosgene absorbed determined by a Mohr's titration for chloride.

The relationship used in determining the pressure quotient from the data:

$$\frac{p_{\mathrm{CCl_4}}}{P - p_{\mathrm{CCl_4}}} = \frac{(\mathrm{CCl_4})}{(\mathrm{CO_2})} = R; \quad \frac{(\mathrm{COCl_2}')}{(\mathrm{CO_2}')} = Q$$

gives

$$K_p = \frac{R}{Q^2} + \frac{R-1}{2Q}$$

of which the latter term may be negligible. The unprimed gas concentrations are for before the reaction; the primed ones are for the gas mixture after reaction.

Experimental

Runs were made with this apparatus at 283°, 314°, 344° and 354°C., both with and without charcoals of different varieties in the tube. The carbon dioxide flow rate was varied between 0.5 and 3.0 cc. per minute. Some runs had to continue for as long as ten hours to yield a sufficient gas sample. In general, the charcoals showed no action, the reaction occurring principally on the Pyrex walls, apparently. We analyzed both gas sampling tubes, each time, and the agreement in the value of Q was generally good, if the conditions had remained uniform, showing that progressive catalyst poisoning was not occurring. New glass and very old glass (Pyrex) both seemed to be active catalytically.

For data by the dynamic method at a lower temperature, a different tube was used—the same one that had been utilized in the attempts to convert phosgene to carbon tetrachloride. It had seen much service, and had crystallized spots, or devitrified, on its inner surface. With otherwise the same apparatus, several runs were made at 250°C.

Many of these runs, in both set-ups, gave low phosgene yields, compared to the rest. These non-equilibrium results were obtained in a quite irregular order, in general, and were not reproducible. In magnitude they extended to perhaps five or ten times the minimum $K(CO_2 \times CCl_4/(COCl_2)^2)$ which was, however, fairly reproducible. The runs in which the maximum phosgene formation was obtained at a given temperature amounted to about one-half the total number, and were relatively fewer at the lower temperatures. It was obvious that the condition of the surface was very important in determining its catalytic effect.

TABLE 8

Experimental results for $CO_2 + CCl_4 = 2COCl_2$

TEMPERATURE	RUN NO.	1/K	WEIGHTED AVERAGE 1/K	+log K	1/T	Q	R
degrees C.							
354	1	331	316	−2.500	0.001595	0.0293	0.303
354	2	305				0.0316	0.310
344	3	450	435	−2.638	0.001620	0.0243	0.277
344	4	456				0.0244	0.284
344	5	394				0.0259	0.278
344	6	437				0.0236	0.252
344	7	437				0.0232	0.244
344	8	411				0.0135	0.0819
344	9	432				0.0120	0.0683
344	10	451				0.0121	0.0721
314	11	1,212	1,280	−3.080	0.001704	0.0130	0.214
314	12	1,116				0.0137	0.214
314	13	1,365				0.0128	0.229
314	14	1,313				0.0131	0.230
283	15	4,900	4,900	−3.690	0.001799	0.00595	0.175
250	16	16,600	17,100	−4.233	0.001911	0.00388	0.253
250	17	17,600				0.00378	0.255
198	18	458,000	452,000	−5.655	0.002120	0.00073	0.244
198	19	442,000				0.00074	0.242

For temperatures below 250°C. the dynamic method was dropped, as the reaction velocity becomes too slow. Two 2-liter Pyrex flasks were thoroughly dried by heating to almost the softening point for an hour and at the same time passing in a stream of dried carbon dioxide. At least one hundred volumes of carbon dioxide were passed through, insuring the removal of air. Then, weighed quantities of carbon tetrachloride in long thin tubes closed at the bottom were introduced and the flasks sealed off, as quickly as possible. They were placed in a constant temperature oven at 198°C. One was removed at the end of 5 days, and the other at 14 days. The same method for the calculation of K was used as for the dynamic method runs, except that R was calculated from the known volume of carbon dioxide and the weight of carbon tetrachloride. Also, in determining Q it was unnecessary to analyze for carbon dioxide, so distilled water was used to decompose the small amount of phosgene formed and absorb the hydrogen chloride. Thus it was unnecessary to eliminate carbon dioxide before proceeding with the Mohr's titration; instead, neutralization with calcium hydroxide was required. The two bulbs gave almost equal values of K, so that an equilibrium was obtained.

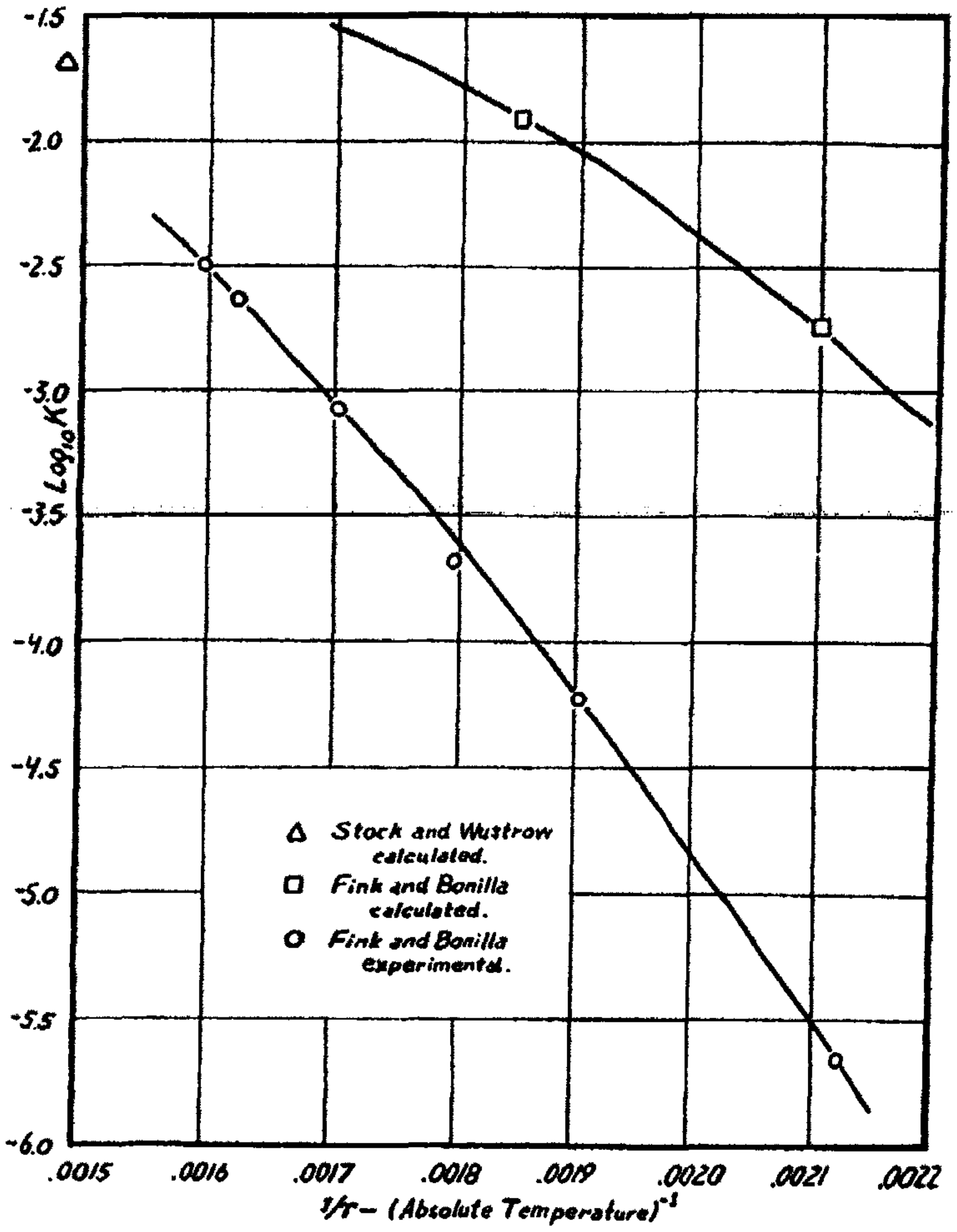

FIG. 7. EXTENT OF THE REACTION $CO_2 + CCl_4 \rightleftharpoons 2COCl_2$

The results obtained by all of these methods are given in table 8. In all of these phosgene formation runs no chlorine was ever noticed, by smell or by the iodide-starch test, owing undoubtedly to the fact that no catalyst for its formation was present. So the reaction was not complicated by the decomposition of carbon tetrachloride or that of phosgene to carbon monoxide and chlorine. Undoubtedly phosgene was formed in every case, as it could be detected by its distinctive smell even in the lowest concentrations. No hydrogen chloride was ever noticed after a run was well started.

The results have been plotted in figure 7, and approach the theoretical curve as the temperature rises. It is noticed that the point at 283°C. does not quite fall on the curve with the rest. This was the lowest temperature at which the first heating coil was used, and probably the corresponding equilibrium was not reached, owing to diminished speed of reaction, that was reached at the higher temperatures. It was practically impossible to operate at flow rates small enough to reach equilibrium at below 300°C. for this first coil, or at below 250°C. for the old tube. Five-tenths of 1 cc. of carbon dioxide per minute was the lowest rate found feasible.

The fact that a different tube, in the case of the point at 250°C. and an entirely new method at 198°C., gave points on a smooth curve that is almost straight seems to bolster up the possibility that a real metastable or false equilibrium is reached in this reaction, which similarly may be true for other reactions; $C + 2Cl_2 = CCl_4$ has already been considered, and $2COCl_2 = (COCl_2)_2$ has been mentioned.

The constant volume small bomb results of Stock (21) are naturally not of the same degree of accuracy as these based on the dynamic method. Stock could only produce a few hundredths of a cubic centimeter of phosgene in a bomb. For the production of carbon tetrachloride by the reverse of the reaction now being considered he has fairly good checks in two runs (31) at 400°C. and two at 500°C. The values of $(COCl_2)^2/(CO_2) \times (CCl_4)$ we obtain from his data are $\log^{-1} 2.77$ at 500°C. and $\log^{-1} 3.77$ at 400°C. These points bear out the false equilibrium theory, but were not plotted in figure 7 because the curves now shown would be dwarfed.

We believe that we have really reached an equilibrium. It may be the end of a fast reaction, with another slow one occurring simultaneously, which will eventually lead the system to the theoretical equilibrium. It is not possible at present to tell whether such a slower reaction exists, but from our data and those of Bodenstein and of Stock it is apparent that such a slower reaction must indeed be slow, compared to the observed one. This statement also holds for the other previously mentioned "false equilibria." In table 9 are given data for runs at 344°C. at higher flow rates than the minimum ones used. The pressure quotient obtained is plotted in figure 8 against the carbon dioxide flowmeter reading, which is practically proportional to the carbon dioxide mass flow at the low flow rates used. It is seen that extrapolation to zero flow rate along the simple curve gives practically the same value for the extent of reaction as that obtained at the lowest flow rate that was actually used. In carrying out the extrapolation it should be remembered that at zero flow rate the curve should approach the pressure quotient axis normally. For simplicity we did not apply this slight correction for finite reaction time, owing to its small magnitude under the conditions and to the additional amount of data that would have been required at the various temperatures. We do not feel that these data are sufficiently accurate to merit calculation of the velocity constant, etc.

TABLE 9

Effect of flow rate variations on the extent of reaction of $CO_2 + CCl_4 = 2COCl_2$ *at 344°C.*

RUN NO.	FLOWMETER	1/K	WEIGHTED AVERAGE 1/K	log K	Q	R
	mm.					
3 to 10	3.4		435	−2.638	0.024	0.26
20	22.0	3,080	2,960	−3.472	0.00885	0.244
21	22.0	2,840			0.00920	0.244
22	16.5	1,090	1,200	−3.080	0.01446	0.234
23	16.5	1,490			0.01259	0.241

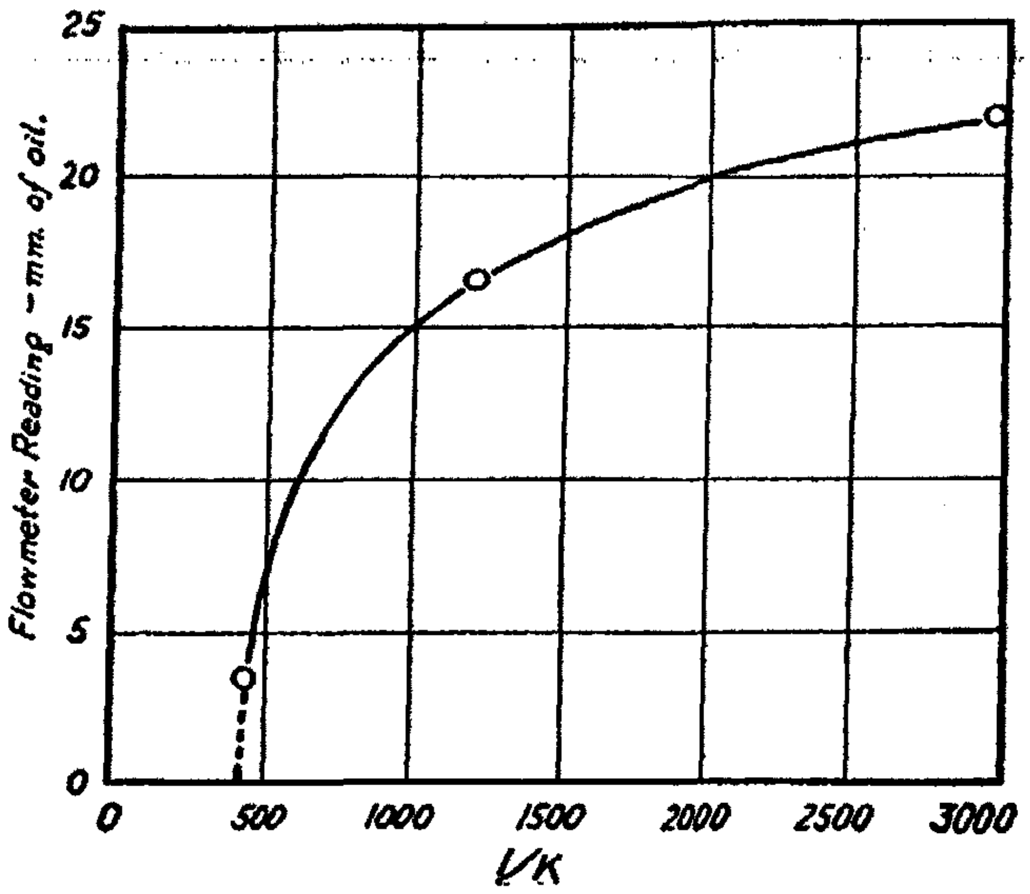

FIG. 8. EFFECT OF FLOW RATE ON THE REACTION $CO_2 + CCl_4 \rightleftharpoons 2COCl_2$ AT 344°C.

A careful consideration of the experimental facts seems to point more strongly to the existence of a false equilibrium of unknown mechanism than to a simple catalyst poisoning, as advocated by Bancroft (31), for false equilibria in bomb reactions. Bancroft does not mention the dynamic method. The principle argument for catalytic surface poisoning in this reaction is given by the consideration that over a rather broad range of gas phase compositions, between the two false equilibrium curves, the forward and reverse reaction velocities are equal, or almost equal if a slight drift towards the true equilibrium exists. It is hard to conceive of this being so unless the two velocities are each zero, or almost so, and the simplest explanation for this would be a poisoned catalyst, unable to allow either forward or reverse reaction to proceed.

In support of some other mechanism as causing the false equilibria let us consider the possible explanations according to the poisoned catalyst theory. False equilibrium might be expected, owing to one of the following phenomena: (1) any one or more of the reactants being strongly and reversibly adsorbed by the catalytic surface (excluding others); (2) any reactant or outside substance being strongly and irreversibly adsorbed, forming a compound of very low dissociation pressure, deactivating the surface. According to the first possibility the reaction velocity would decrease rapidly but smoothly as the pressure of the strongly adsorbed substance increased. However, the composition of the gas phase in equilibrium with the catalyst could not vary, according to the principles of thermodynamics, or, to be more accurate, the equilibrium pressure-constant calculated for the gas phase cannot depend on the nature of the catalyst surface. Our value of the pressure quotient therefore does not depend on the reversible absorption of one of the reactants, assuming equilibrium to have been practically reached. Furthermore, if the reaction velocity in one direction were decreased by stronger adsorption of the product, that in the opposite direction with the same catalyst would be increased, and none of the reactions have been found to take place as readily as this would indicate. For instance, the same tube that was utilized for the reaction $CO_2 + CCl_4 = 2COCl_2$ at 250°C. gave no indication whatsoever of the reverse reaction, as has already been mentioned. The second above possible explanation obviously cannot be true in this case, in which the extent of reaction was never found to vary consistently with the age of the catalyst, or length of the run.

To supply somewhat of a check on the results, runs 8 to 10 were performed, in which the relative amounts of the gases in the issuing equilibrium mixture were varied by cooling the carbon tetrachloride evaporator. Compared to runs 3 to 7, at the same temperature and flow rate, the equilibrium phosgene concentration has decreased to about one-half and the carbon tetrachloride concentration to about one-fourth of the values for the previous runs. The pressure quotient K is seen to remain the same, in fact the average K's for the two groups of runs are so similar that the agreement is partly fortuitous, as can be told from the magnitude of the individual deviations.

A third possible explanation of the results obtained is that one of the products, say phosgene, might reversibly combine with the solid catalyst to form a solid compound, of appreciable dissociation pressure, that has no catalytic properties. There would, from the phase rule, be only one equilibrium pressure of phosgene at any temperature, if both solid phases were present. Therefore it would not be possible to produce the poison phosgene, say, at a pressure higher than this pressure for equilibrium with the poisoned catalyst, and one would be measuring the dissociation pressure of this poisoned catalyst rather than the gas reaction equilibrium. This state of affairs would also give the same false equilibrium with the streaming method as with bomb reactions. However, this is probably not the explanation in this case, as many factors oppose it. In the first place, the same catalyst could not cause each of two opposing reactions to take place, separately, even to a slight extent, as Stock has succeeded in doing for the forward and reverse reactions of $CO_2 + CCl_4 = 2COCl_2$. In the second place, the calculated K would vary as the initial ratio R were varied, whereas runs 8 to 10 show no variation. Finally, if such a poisoned catalyst compound is formed, a little reasoning will show that a smooth curve of flow rate (or time of reaction) against K or fraction decomposed would not be obtained; there would be a discontinuity at the flow rate at which the time of reaction were just sufficient for the reaction to have proceeded to the point where the phosgene pressure produced equaled the poisoning phosgene pressure. Figure 8 seems to indicate that this is not so, although obviously there are not enough points to make the argument strong.

SUMMARY

We have investigated several little-known reactions by which carbon tetrachloride might be commercially produced. With this purpose in mind we have coördinated the previous work in this field and carried out similar and other experiments of our own.

We have concluded that a number of these reactions, generally chlorinations of carbon compounds or of carbon itself, and other related reactions, differ inherently in the manner in which they occur, from those between carbon and oxygen, sulfur, or even hydrogen. A great deal of further work is necessary to clear up the subject.

A detailed summary follows:

Theoretical calculations

1. A series of new thermodynamic data has been calculated from available data. The results include C_p of carbon tetrachloride vapor at 1 at-

mosphere from 0°C. to 300°C., S_{298} of silicon dioxide (quartz), $C_{p,298}$ of phosgene at 1 atmosphere, and $\Delta F°_{298}$ of formation of silicon tetrachloride (g), stannic chloride (g), aluminum chloride (g), and silicon dioxide (quartz).

2. The equilibrium constant for the reaction $2CCl_4 = C_2Cl_4 + 2Cl_2$ was calculated from experimental data of Weiser and Wightman.

3. A convenient and accurate method was developed for obtaining the equilibrium constant of the reaction, $CO_2 + CCl_4 = 2COCl_2$, involving saturating carbon dioxide with carbon tetrachloride at a known temperature and analyzing the equilibrium mixture for $(COCl_2)/(CO_2)$ ratio.

Experimental work

4. It was shown theoretically and supported experimentally that it is not possible to carry out appreciably the reaction $COCl_2 + 2MeCl = CCl_4 + Me_2O$, where Me is an equivalent of a metal. Ultra-violet light was shown to displace the equilibrium, in one case, towards the right.

5. Ordinary animal charcoal was found to be a good catalyst for the reaction $CCl_4 = C + 2Cl_2$, but experimental confirmation could not be obtained of the reverse reaction.

6. The reaction $2COCl_2 = CO_2 + CCl_4$ was attempted in both directions and the reverse reaction quantitatively studied, and indications were obtained of the existence of an undetermined factor which prevents the reaching of the theoretical equilibrium.

7. A new method for the volumetric analysis of carbon tetrachloride mixed with other gases was developed, tested and found satisfactory. Also, a method for the continuous absorption of chlorine, phosgene and carbon dioxide and determination of their proportions was devised and found satisfactory.

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ON THE MECHANISM OF GASEOUS REACTIONS. I

The Thermal Decomposition of Methyl Ethyl Ether

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In recent years a great deal of attention has been focussed on the study of the kinetics of homogeneous gaseous reactions, in particular those of thermal decomposition processes. In a considerable number of cases it has been found that the rate follows a first order equation which corresponds to a unimolecular mechanism. As a general rule the more complex molecules tend to decompose at a unimolecular rate, and the field of organic chemistry has proved particularly fruitful in providing examples. Accurate measurements of rates have led to the development of a number of theories regarding the mechanism of the activational process, the most successful of which have made use of energy supplied at molecular collisions, taking into account the internal degrees of freedom of the molecules (1). The decrease in rate when the pressure is lowered, which is characteristic of a number of unimolecular reactions, is a necessary consequence of such theories. The radiation hypothesis (2), which ascribed activation to the absorption of infra-red radiation by the molecules of the reactant, in its general form unfortunately permits of no comprehensive experimental test, largely on account of the difficulties connected with manipulation in the infra-red (3).

In many of the reactions studied the problem of working out the kinetics of the process is complicated by the fact that there may be several ways in which the molecule can break up, and the decomposition is not a single reaction but involves concurrent and consecutive processes. It is often possible, however, either to neglect or to correct approximately for these complications, since one reaction may predominate as the rate-determining step. This is fairly satisfactory where side reactions involve only a small fraction of the reacting substance, and where subsequent processes are either too slow or too fast to interfere with the primary rate, but this of course cannot always be the case. Where reactions are studied over wide ranges of temperature and pressure, the relative effects of the various processes involved may vary considerably, and this may invalidate conclusions of a theoretical nature which are based on the assumption of a single reaction mechanism.

It is therefore of considerable importance that deviations from simple uni- or bi-molecularity be investigated with regard to the possibility of complicating reactions, and the kinetics of the various processes be worked out where possible. One such case has been studied by Clusius and Hinshelwood (4), in the catalytic decomposition of diethyl ether.

The present article deals with a study of the decomposition of methyl ethyl ether, in which case marked deviations from a simple unimolecular course have been observed. This decomposition has been studied by Glass and Hinshelwood (5), who noted approximate unimolecularity but state that "the reaction is far from being an ideal example of a unimolecular change." The results here reported disagree in some respects with those of these two authors, our rates being uniformly lower. We have noted, however, a marked catalytic effect produced by the presence of small quantities of alkyl iodide such as may be introduced into the ether during its preparation. The second article of this series will deal with this phase of the work.

EXPERIMENTAL

The course of the decomposition process was followed by observing the pressure increase when samples of the gas were maintained at constant temperatures and volume in a Pyrex glass reaction tube.

Apparatus

The experimental arrangements are shown diagrammatically in figure 1. Vessels A, B, and C constitute a train for the preparation and purification of the ether, and D is a storage flask of 1-liter capacity provided with the manometer M_2. Several reaction chambers, E, were used, these being of Pyrex with about 125-cc. capacity. Connection with the storage flask was provided at stopcock T_1, and with diffusion or Töpler pumps at T_2, all connecting tubing being of capillary size. Pressures were measured on the constant-volume manometer H operated by the levelling device G. The gas space outside the furnace was small compared with the total. An electric furnace was used for heating, and the fluctuations in line voltage during a run were compensated by the use of a slide wire resistance operated by hand. Since the furnace and reaction tube were heated for two to three hours prior to each run, the above method of regulation was found to be quite satisfactory. Temperatures were measured by the platinum resistance thermometer I, in some cases a thermocouple being inserted as a check. For the early runs the temperature variation was of the order of 2°C., while for later runs on which most of the conclusions are based the temperature was controlled to within 0.8°C. The absolute values of the temperature are probably correct to 2°C.

Since there is always some uncertainty in obtaining the initial pressure of gas by direct measurement, it was found to be more satisfactory to continue each experiment until a constant final pressure was recorded and to use this value to obtain the initial pressure. The ratio of initial to final pressures was determined accurately at several temperatures by admitting gas to the cold reaction chamber, followed by heating until decomposition was complete. It turned out that this ratio was constant over the temperature range employed.

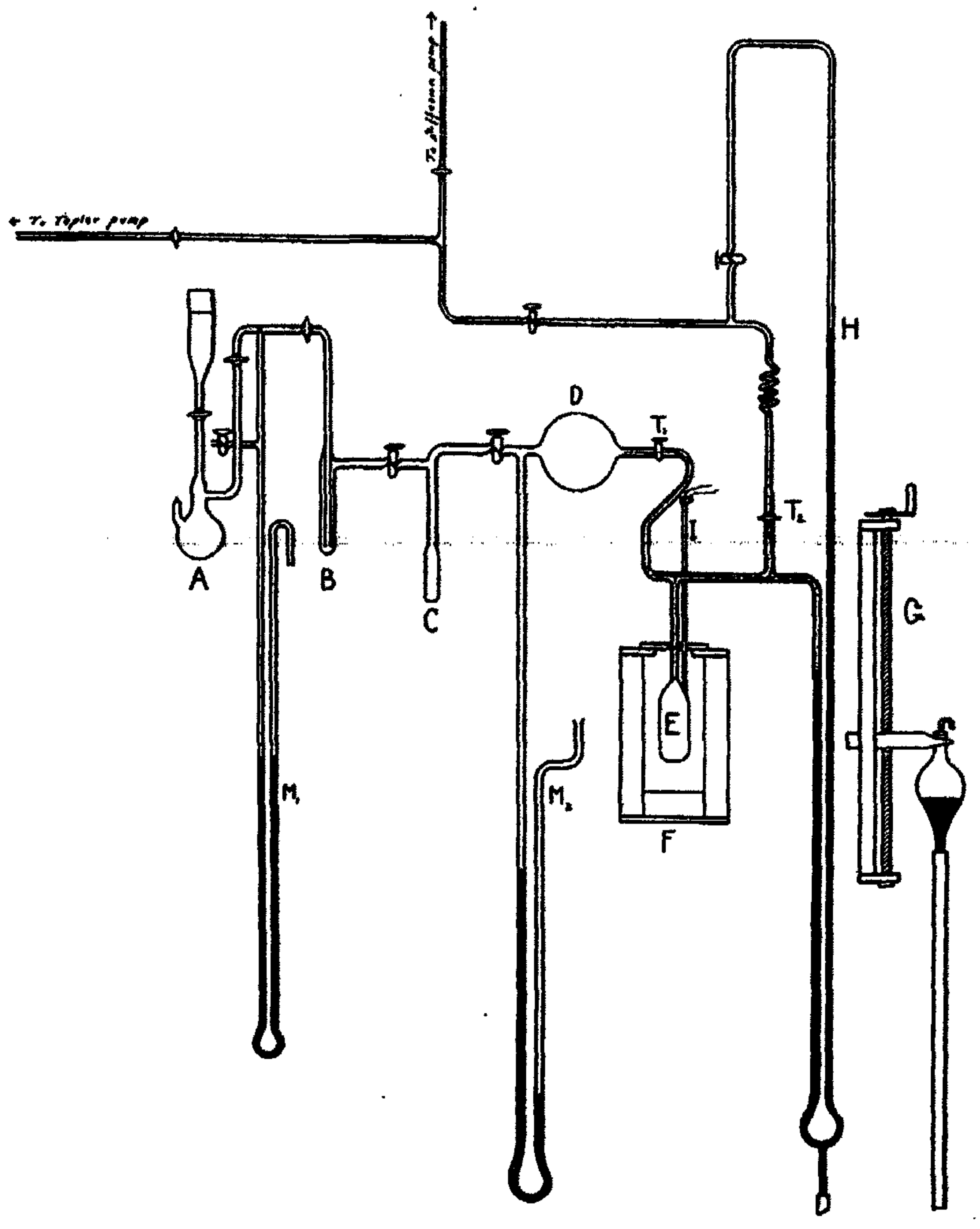

Fig. 1

Preparation of the ether

Methyl ethyl ether was prepared according to the historic method of Williamson (6), by allowing sodium methoxide to react with ethyl iodide, followed by distillation. Several samples were prepared, and modifications of procedure and apparatus were introduced to improve yield and purity of product. A number of rate measurements were made on samples prepared under various conditions, and it was observed that rates varied considerably from sample to sample. The discrepancy was traced to the presence in the final product of small quantities of ethyl iodide, which were found to exert a marked catalytic effect on the decomposition rate. The procedure finally adopted to ensure the elimination of ethyl iodide was as follows (sample 5): Eight grams of sodium were allowed to react completely with 75 cc. of absolute methyl alcohol. The resulting solution of sodium methoxide in the excess alcohol was run into the flask A, which had previously been evacuated. A quantity of ethyl iodide (23 cc.) less than the calculated amount was then admitted and the mixture allowed to stand for 6 days. It was then heated to 45°C. and a fraction of about 7 cc. distilled over into tube B, which was immersed in liquid air. Here the distillate came in contact with metallic sodium which served to remove methyl alcohol. Tube B was warmed to room temperature and some gas released through the stopcock at the manometer. The ether was then condensed in tube C at -10°C., cooled with liquid air, and permanent gases pumped off. The product was distilled back into tube B for further treatment with sodium, returned to C, cooled in liquid air once more, and the system evacuated. The ether was then allowed to expand into the reservoir. With the above quantities a pressure of 60 cm. at room temperature was obtained.

Analysis of the products of reaction

The gas mixture from the reaction chamber was pumped off with the Töpler pump, collected in a gas burette over water (or over mercury in the cases of partial decomposition), and the constituents determined in the usual manner. Undecomposed ether was determined by absorption in cold concentrated sulfuric acid, hydrogen by palladinized asbestos or copper oxide; in the latter case the gas mixture was passed slowly back and forth over the oxide at 280°C. ten or twelve times. Methane and ethane were determined by explosion.

To detect the presence of aldehydes in the gases from incomplete decomposition the silver mirror test was applied to a few cubic centimeters of water which had been standing in contact with the gas. To distinguish between formaldehyde and acetaldehyde the gas mixtures were allowed to stand in contact with about 10 cc. of ethyl alcohol in the Töpler pump. A portion of this solution was then tested for acetaldehyde by heating with sodium hydroxide. Even small concentrations of acetaldehyde produce a yellow color and distinctive odor (7). For formaldehyde, heating a portion of solution with 0.05 g. of resorcinol and 50 per cent sodium hydroxide produced a pink shade (8). Estimation of quantities in both tests was made by color comparison with known solutions.

RESULTS

The products of the reaction

The complex nature of the decomposition process may be seen from the diversity of the products as given in table 1. Here are shown the percentages of the various constituents found in the gas mixture after the reactions had been carried to completion. The discrepancies in the totals may be due to the small volumes analyzed in some cases. The presence of considerable hydrogen in all cases is interesting, since Glass and Hinshelwood report no hydrogen. The gas mixture shows approximately the same composition at the different temperatures of decomposition, and is much the same for the different samples of ether prepared, although as mentioned above there is reason to believe that the decomposition process was somewhat different in the cases of samples 2, 3, and 4, than for sample 5.

TABLE 1

Products of the thermal decomposition of methyl ethyl ether

TEMPERATURE	ETHER SAMPLE	CARBON DIOXIDE	UNSATURATEDS (C_2H_4)	OXYGEN	CARBON MONOXIDE	HYDROGEN	METHANE	ETHANE	TOTAL
degrees C.		*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	
509	2	2.2	4.0	0	28.3	5.7	53.8	2.0	96.0
510*	3	0	0	1.0	33.3	1.1	55.7	4.7	95.8
456	4	0	4.0	0.8	30.8	4.0	55.6	4.7	99.9
457	5	0	5.1	0.8	33.1	8.4	45.2	6.5	99.1
487	5	2.9	0.7	0.7	31.8	9.8	52.7	4.4	103.0
509	5	0.2	1.8	0.5	32.0	9.4	50.5	5.6	100.0

* Reaction bulb packed with glass rods.

In a series of experiments the gas was removed from the reaction chamber before the reaction was complete, in order to obtain evidence of the presence of aldehydes as intermediate products, and to compare the other products with those obtained at the end of the reaction.

While both formaldehyde and acetaldehyde were detected the concentration of the former was always very small, while that of the acetaldehyde was appreciable. Thus when the pressure had increased by 50 per cent at 490°C., the pressure of formaldehyde in the reaction chamber was estimated at 0.08 cm., and that of acetaldehyde at 14.5 cm. At 565°C. at a pressure 2.3 times the initial there was found a trace of formaldehyde and about 5 cm. of acetaldehyde. The proportions of the other constituents in some of these experiments are shown in table 2.

As a result of these analyses the steps in the decomposition process would appear to be the following:

$$CH_3OC_2H_5 \rightarrow CH_3COH + CH_4 \tag{1}$$
$$CH_3OC_2H_5 \rightarrow HCOH + C_2H_6 \tag{2}$$
$$CH_3COH \rightarrow CH_4 + CO \tag{3}$$
$$HCOH \rightarrow H_2 + CO \tag{4}$$
$$C_2H_6 \rightleftharpoons C_2H_4 + H_2 \tag{5}$$

Reaction 1 followed by reaction 3 seems to be the predominating process, the analyses indicating that about 65 per cent of the ether decomposes according to reaction 1 at all temperatures. The decomposition of the formaldehyde according to equation 4 appears to be fast compared with that of the ether, while that of acetaldehyde may be relatively slow, as shown by the concentrations of this compound obtained during the course of the reaction. The equilibrium between ethane and its products (equation 5) accounts for the presence of ethylene, and it is to be expected that this equilibrium would be established in the temperature range used (9).

TABLE 2

Products of the partial decomposition of methyl ethyl ether (sample 5)

TEMPERATURE	ETHER SAMPLE	ETHER	CARBON DIOXIDE	UNSATURATEDS (C_2H_4)	OXYGEN	CARBON MONOXIDE	HYDROGEN	METHANE	ETHANE	TOTAL
degrees C.		*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	
400	5	24.3	0	6.8	1.0	32.2	5.1	37.9	11.6	94.6
486	5	11.9	0	1.7	0.6	31.2	7.5	52.5	7.9	101.4
507	5	26.4	0	4.5	1.2	38.7	8.3	41.2	3.2	96.4

The above processes produce somewhat over three moles for one, so that the pressure at the end of the reaction should be over three times the initial pressure. It was found, however, that the final pressure was only 2.70 times the initial at a series of temperatures within the range of the experiments. This means that some non-gaseous products are formed, the nature of which has not been determined. Whether these are formed from the original ether or from the intermediate products is not evident from the results, but since the extent of this condensation seems to be independent of temperature it will not greatly affect the conclusions here obtained.

The kinetics of the decomposition

That the reaction as a whole is approximately a first order process in most cases is illustrated in table 3, which shows a summary of the majority of the complete runs which were carried out. The columns headed t_{25}, t_{50}, and t_{75} show the time in minutes for the pressure increase to reach 25 per cent, 50 per cent, and 75 per cent, respectively, of its final value. The last three columns show the ratios $t_{25}:t_{50}:t_{75}$, with t_{50} taken as unity. For a unimolecular process these ratios should be 0.415:1:2, while for a bimolecular they should be 0.333:1:3. The numbers corresponding to the sample of ether from which the gas sample was drawn are shown in the second column. The time values vary remarkably from sample to sample at corresponding temperatures and those for sample 5 are the largest, indicating the slowest rates. This variation as mentioned above has been shown to be attributable to the presence in samples 2, 3, and 4 of traces of ethyl iodide acting as a catalyst.

TABLE 3

Summary of the majority of the complete runs

NO.	ETHER SAMPLE	TEMPERATURE	INITIAL PRESSURE	t_{25}	t_{50}	t_{75}	$t_{25}:t_{50}:t_{75}$
		degrees C.	*cm.*	*minutes*	*minutes*	*minutes*	
4	2	503	11.92	7.4	15.0	32.5	0.493:1:2.16
5	2	509	7.7	7.5	18.9	40.4	0.397:1:2.14
8	3	510	17.3	1.0	2.1	4.0	0.476:1:1.91
9*	3	510	15.1	2.5	30.6	110.2	0.082:1:3.60
10†	3	510	14.7	4.7	12.5	40.0	0.376:1:3.20
12†	3	487	14.4	5.0	13.5	31.8	0.370:1:2.36
14	3	487	13.4	2.4	5.3	10.4	0.453:1:1.93
15	3	487	3.2	7.4	15.9	30.0	0.465:1:1.89
16	4	456	10.25	8.9	29.5	64.7	0.302:1:2.19
30	5	457	29.66	151.4	377.6		0.401:1: —
25	5	487	24.96	28.6	66.7	146.3	0.429:1:2.20
29	5	488	30.44	25.8	66.4	169.2	0.389:1:2.55
26	5	509	29.9	13.8	34.3	91.0	0.402:1:2.65
37	5	510	23.6	12.3	33.0	89.5	0.373:1:2.71
32	5	565	28.7	0.77	2.32	8.0	0.331:1:3.45

* Bulb packed with glass wool.

† Bulb packed with glass rods.

Runs 9, 10, and 12 were made with the reaction chamber packed with glass wool or glass rods and show a marked decrease in rate, which is connected with the catalytic behavior.

In interpreting the mechanism of the decomposition process, only those experiments made with ether sample 5 will be considered here, for the reasons advanced above. The treatment of the catalyzed reaction will be taken up later.

It was first noticed that at the lowest temperature used the process is very closely a unimolecular one. This is shown in table 4 for an experiment at 457°C. The pressures given in the second column were taken from a smoothed curve of the experimental data which was extrapolated back to the initial pressure for zero time, and the values of the unimolecular constant k_1 are calculated over 20-minute intervals. This may be interpreted as meaning that the rate-determining step at 457°C. is the primary decomposition of the ether, and the subsequent reactions are rapid. That is, the decomposition even of the acetaldehyde is fast compared with that of the ether.

TABLE 4

Decomposition of the ether at 457°C.

Initial pressure, 29.66 cm.

t	P	$k_1 \times 10^3$
minutes	*cm.*	*min.*$^{-1}$
0	29.66	
20	31.30	1.65
40	33.05	1.82
60	34.75	1.84
80	36.45	1.91
100	38.15	1.99
120	39.85	2.07
140	41.45	2.01
160	42.90	1.92
180	44.30	1.91
200	45.60	1.85
220	46.80	1.77
240	48.00	1.83
260	49.15	1.82
280	50.30	1.90
300	51.40	1.88
320	52.40	1.77
340	53.35	1.75
360	54.20	1.61
380	54.95	1.46
400	55.65	1.42
		Av. = 1.81

As the temperature is raised, however, this is no longer the case, and the higher the temperature the greater the deviation from the simple mechanism. This is shown in figure 2 in which log $(P_f - P)$ is plotted against the time for a number of runs, where P_f is the final pressure and P the pressure as measured throughout the course of the reaction. For a unimolecular reaction of course this plot should give a straight line, and this is practically the case at 457°C. At 487°C. the deviation is not very great, the calculated constant first increasing and then decreasing during the course of the reaction. The values at this temperature are given in table 5.

The greatest deviation is shown in the experiments at 565°C., and here calculation shows that the rate-determining step is practically bimolecular. This is shown in table 6 where the bimolecular constant is obtained from the values of $\frac{1}{P_f - P}$ throughout the reaction. In this case a correction has been applied to the value of P_f to take into consideration the subsequent decomposition of ethane, which is apparently much slower than the main process.

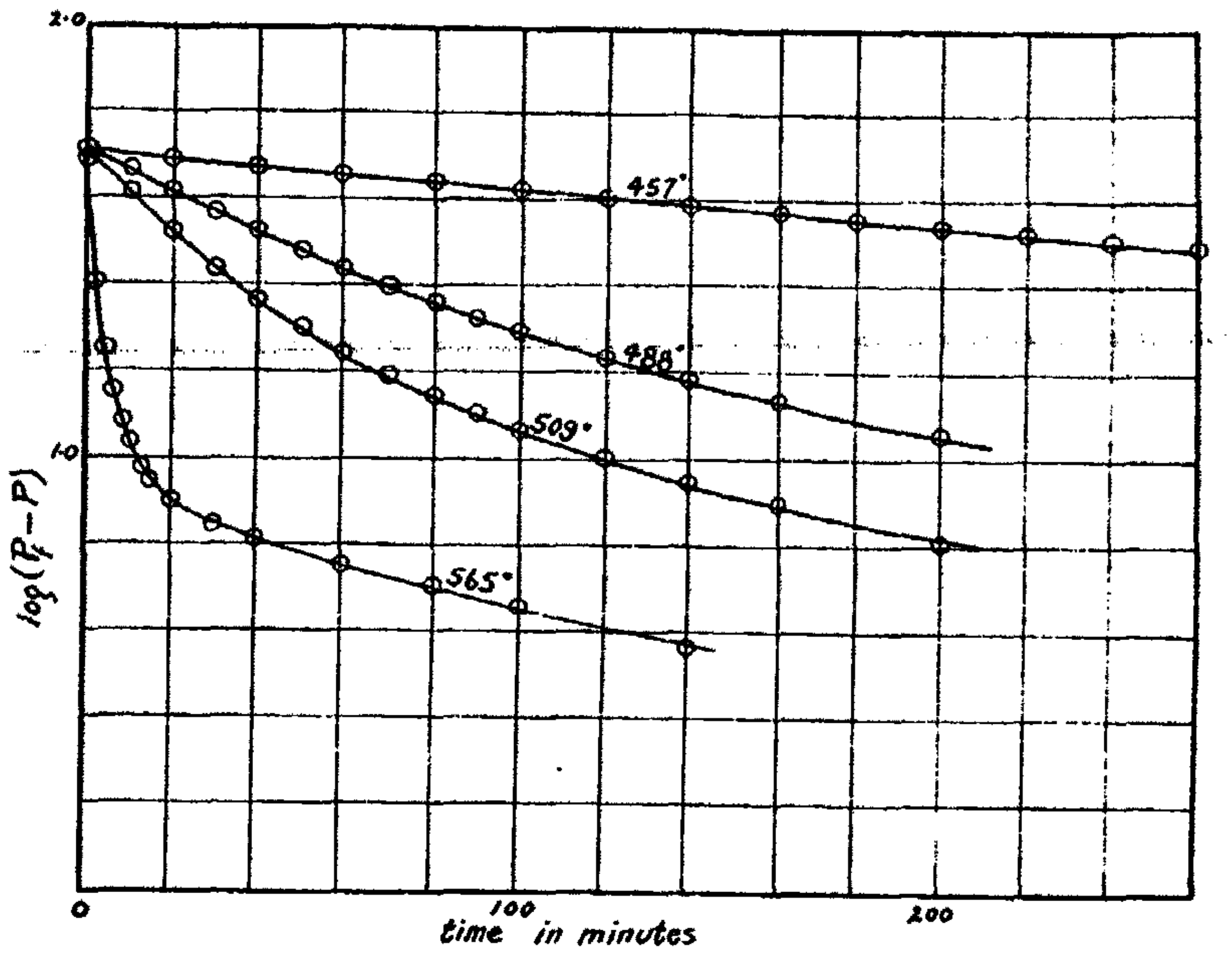

FIG. 2

The bimolecular decomposition of acetaldehyde has been studied by Hinshelwood and Hutchison (10) and the value of the constant at 565°C. taken from the work of these authors is shown in the table. k_2 as obtained here is considerably smaller, but of the same order of magnitude.

The explanation of this bimolecular rate is then that the decomposition of acetaldehyde is the rate-determining step, the primary decomposition of the ether taking place very rapidly by comparison, so that in the early stages of the process the ether is practically completely decomposed.

TABLE 5

Decomposition of the ether at 487°C.

Initial pressure, 24.96 cm.

t	P	$k_1 \times 10^2$
minutes	*cm.*	*min.*$^{-1}$
0	24.96	
10	28.85	0.96
20	32.60	1.02
30	36.10	1.06
40	39.25	1.06
50	42.17	1.09
60	44.73	1.07
70	46.85	0.95
80	48.68	0.96
90	50.25	0.87
100	51.63	0.83
120	53.87	0.76
140	55.68	0.72
160	57.30	0.74
200	59.60	0.64

TABLE 6

Decomposition of the ether at 565°C.

Initial pressure, 28.7 cm.

t	P	$P_f - P$	$k_2 \times 10^2$
minutes	*cm.*		*cm.*$^{-1}$ *min.*$^{-1}$
0	28.7	44.95	
1	40.8	32.85	0.82
2	52.1	21.55	1.59
3	56.7	16.95	1.26
4	59.85	13.80	1.34
5	61.95	11.70	1.31
6	63.4	10.25	1.20
7	64.5	9.15	1.19
8	65.4	8.25	1.19
9	66.15	7.50	1.21
10	66.8	6.85	1.26
15	68.8	4.85	1.20 Av. = 1.23
20	69.7	3.95	0.94
30	70.6	3.05	0.75

Final pressure of ethylene taken as 4 cm. k_2 for acetaldehyde at 565°C. (Hinshelwood and Hutchison) = 2.09×10^{-2} cm.$^{-1}$ min.$^{-1}$

At intermediate temperatures both processes should be proceeding at measurable rates, and the process then consists in the main of a unimolecular reaction followed by a bimolecular one. Such a mechanism does not permit of simple mathematical treatment, but an attempt has been made to obtain a certain correlation of the results.

The total pressure P at any time t during the reaction will on the assumptions outlined above be given by

$$P = P_f - (P_f - P_i)\, e^{-k_1 t} - b \tag{1}$$

where P_f is the final pressure, P_i the initial pressure, k_1 the unimolecular constant for the total ether decomposition, and b the pressure due to the acetaldehyde present. Here the formation of condensed products if from the original ether is assumed to be a first order process; if from intermediate products then the rate must be fast. The formation of ethylene from ethane is not taken into consideration, but if this takes place only at a later stage in the process, then the value of P_f in the above equation will have to be modified accordingly.

Now the pressure due to acetaldehyde is changing at the rate given by

$$\frac{db}{dt} = 0.65\, k_1\, P_i e^{-k_1 t} - k_2 b^2 \tag{2}$$

where 0.65 k_1 represents the part of the rate constant which refers to the decomposition of the ether to acetaldehyde, and k_2 is the bimolecular constant for acetaldehyde.

Equation 2 unfortunately has no finite solution, so that it is necessary to make use of it in the differential form.

Differentiating equation 1 we obtain

$$\frac{dP}{dt} = k_1\, (P_f - P_i)\, e^{-k_1 t} - \frac{db}{dt}$$

and combining with equation 2,

$$\frac{dP}{dt} = k_1\, (P_f - 1.65\, P_i)\, e^{-k_1 t} + k_2 b^2 \tag{3}$$

Now the value of k_1 may be estimated from the following considerations. Near the beginning of the process b is very small and hence $k_2 b^2$ in equation 3 may be neglected. This equation integrated then gives

$$P = (P_f - 0.65\, P_i) - (P_f - 1.65\, P_i)\, e^{-k_1 t}$$

or

$$\log\, (P_f - 0.65\, P_i - P) = \log\, (P_f - 1.65\, P_i) - \frac{k_1}{2.303}\, t \tag{4}$$

k_1 may then be obtained from a series of the values of P near the beginning of the reaction for which equation 4 is linear.

Having k_1, values of b throughout the reaction are obtained from equation 1, and then values of k_2 from equation 3, making use of slopes of tangents to the experimental pressure-time curve to obtain $\frac{dP}{dt}$.

The results of applying this method of treatment to an experiment at 509°C. are shown in table 7.

The value of k_1 using equation 4 comes out to be 0.0387. The second column shows the experimental values of total pressure throughout the experiment. Values of b and k_2 are obtained using equations 1 and 3. The column headed P_e gives the pressure due to undecomposed ether at the corresponding times, the values being obtained from the first order equation

$$P_e = P_i e^{-k_1 t}$$

TABLE 7

Decomposition of the ether at 509°C.

Initial pressure, 29.9 cm.; k_1 = 0.0387 min.$^{-1}$

	P	P_e	b	$k_2 \times 10^2$
minutes	*cm.*	*cm.*	*cm.*	*cm.$^{-1}$ min.$^{-1}$*
0	29.90	29.90	0	
10	39.50	20.30	5.70	4.4
20	47.40	13.80	8.20	2.47
30	53.25	9.38	9.45	1.64
40	57.50	6.38	10.00	1.16
50	60.65	4.31	10.15	0.90
60	63.12	2.94	9.88	1.13
70	65.10	2.00	9.40	1.07
80	66.69	1.38	8.81	1.16
90	67.99	0.94	8.21	1.27
100	69.03	0.62	7.67	1.26
120	70.63	0.29	6.61	1.29
140	71.85	0.13	5.64	1.51
160	72.8	0.06	4.80	1.76
200	74.29	0.03	3.36	1.68

Corrected final pressure taken as 77.7 cm. k_2 for acetaldehyde at 509°C. (Hinshelwood and Hutchison) = 4.37×10^{-2} cm.$^{-1}$ min.$^{-1}$

The values of k_2 show a marked decrease during the initial stages of the reaction and then remain fairly constant. The method involves uncertainties in the assumption that 65 per cent of the ether decomposes to acetaldehyde, and in the effects of the condensation reaction and the formation of ethylene. The value of k_1 may be in error to some extent, and there is the difficulty of obtaining slopes graphically of sufficient accuracy to give reliable results when relatively small differences have to be taken. In view of all this, the conclusions as to mechanism would seem to be fairly well justified by the agreement shown.

The mechanism here outlined involves the assumption that the temperature coefficient of the ether decomposition reaction is considerably larger than that for the aldehyde. The value of E, the critical increment for acetaldehyde, is 45,500 calories per mole, while for the decomposition of methyl ethyl ether, Glass and Hinshelwood give a value of 47,000 calories. Since the results given here are in definite disagreement with the results of these two authors with regard to the magnitude of the rates themselves, it is to be expected that the value of the temperature coefficient will also differ. The rate constants obtained here lead to a value of E of 65,300 calories per mole. Although, owing to the uncertainties entering into the method of treatment, this figure may be somewhat in error, E is apparently much larger than that given by Glass and Hinshelwood.

TABLE 8

Decomposition of the ether at 565°C.

Initial pressure, 28.7 cm.; k_1 = 0.603 min.$^{-1}$

t	P	P_e	b	$k_2 \times 10^3$
minutes	*cm.*	*cm.*	*cm.*	*cm.*$^{-1}$ *min.*$^{-1}$
0	28.7	28.7	0	
1	40.8	15.7	8.35	1.35
2	52.1	8.59	8.15	1.49
3	56.7	4.70	9.62	1.21
4	59.85	2.57	9.79	1.19
5	61.95	1.41	9.51	1.03
6	63.4	0.77	8.95	1.04
7	64.5	0.42	8.49	1.07
8	65.4	0.23	7.89	1.23
9	66.15	0.13	7.30	1.18
10	66.8	0.07	6.74	1.12
15	68.8	0.003	4.85	1.06
20	69.7	0.0002	3.95	0.64

The above value is consistent with the results obtained at the highest temperature, 565°C., as is shown in table 8. Here equation 4 may not be relied upon to obtain k_1, since the decomposition of the aldehyde is appreciable even near the start. k_1 was therefore obtained by extrapolation using the temperature coefficient. Values of b and k_2 were obtained using equations 1 and 3 as in table 7. The column headed P_e shows the pressure of undecomposed ether present at the times given, as calculated from the value of k_1. The agreement between the bimolecular constant obtained here and that in table 6 is quite good.

SUMMARY

1. The decomposition of methyl ethyl ether has been studied over a wide range of temperature and is shown to be a complex process consisting in the main of a unimolecular decomposition of the ether into acetaldehyde and methane, followed by the bimolecular decomposition of the acetaldehyde.

2. These two steps may be treated separately at high and low temperatures, owing to the difference in the two temperature coefficients.

3. A method of treatment of the process at intermediate temperatures has been developed, and values of the rate constants at various temperatures have been obtained.

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ON THE MECHANISM OF GASEOUS REACTIONS. II

Homogeneous Catalysis in the Decomposition of Methyl Ethyl Ether

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During the course of a series of experiments on the thermal decomposition of methyl ethyl ether, some anomalies were observed in the measured rates where different preparations of the ether were used (1). Under the same conditions of temperature and pressure different samples of the gas showed widely different rates. It was suspected that the presence of some impurity in varying amounts was producing a catalytic effect. Since the ether was prepared from sodium methoxide and ethyl iodide, a likely impurity in the product would be the latter substance, and in some of the experiments a brownish deposit, probably iodine, was observed in the capillary tubing above the furnace enclosing the reaction flask. Clusius and Hinshelwood have shown that the alkyl iodides will produce homogeneous catalysis in the case of the decomposition of several ethers, the catalytic effect being largely due to iodine vapor formed by the decomposition of the halide (2).

Since it was desired to study the decomposition of methyl ethyl ether in absence of catalysts, the method of preparation was modified in such a way as to ensure the virtual absence of any iodide in the product. The results of this work have been given in the previous communication of this series.

A few experiments have been carried out for the purpose of substantiating the conclusion that the observed discrepancies in rates were due to catalysis by the alkyl halide, and these are reported here. The results of some calculations as to the mechanism of the catalytic process are also given, since, as in the case of the uncatalyzed decomposition, consecutive reactions appear to be involved.

EXPERIMENTAL

The apparatus employed was the same as that used in the previous work except for the addition of a small bulb containing ethyl iodide. In carrying out a rate measurement a small quantity of ethyl iodide vapor was first admitted to the hot reaction chamber, and heated for a few minutes before the sample of ether was introduced. This should ensure complete decomposition of the iodide at these temperatures (2). Since in previous experiments where catalysis was suspected, the residual gas after decomposition showed approximately the same composition as that obtained in the uncatalyzed process, the gas mixture from the experiments in which ethyl iodide was added was not analyzed, and it was assumed that the reactions taking place were substantially the same as those in the previous cases.

RESULTS

The effect of the addition of ethyl iodide is to produce a marked increase in rate, as may be seen from the values given in table 1. In fact, in run 33 where the highest concentration of iodide was used, the pressure increase was so rapid that it was impossible to obtain pressure readings until the reaction was substantially complete. In the table t_{50} represents the time in minutes for the pressure increase to reach one-half of its final value, and in the case of a single unimolecular reaction these values would be inversely proportional to the reaction rate constant. The reactions here are more complex, nevertheless the time values give an approximate idea of relative rates. Run No. 25 shows the time for the uncatalyzed reaction. The same preparation of ether (sample 5) was used in all of these experiments. The fourth column gives the pressure in the reaction chamber just before the ether was admitted, this being due to the decomposition products of ethyl iodide. Since the connecting tubes outside the furnace were not heated some iodine would condense in these, as was observed in run 33. For this reason the concentrations of catalysts cannot be accurately compared. However it is evident from run 35 that even a small quantity of iodide produces a considerable acceleration.

TABLE 1

The effect of ethyl iodide upon the rate of decomposition of methyl ethyl ether

NO.	TEMPERATURE	INITIAL PRESSURE	PRESSURE DUE TO IODIDE	t_{50}
	degrees C.	*cm.*	*cm.*	*minutes*
25	487	24.96	0	66.7
33	487	11.4	9.1	(0.5)
34	487	24.1	2.5	1.14
35	480	26.95	0.06	9.17

In table 2 are given the time values for experiments carried out with several preparations of ether at various temperatures, showing the great differences obtained. The effect of the variation of the initial pressure (and consequent variation in the concentration of the catalyst) is well shown in the second and third lines where a decrease in pressure to one-fifth of its value decreases the rate approximately three times. The time values for sample 5 represent the rates for the uncatalyzed process, since it is believed that this preparation of ether was virtually free from iodide. The last line refers to one of the experiments (run 35) in which iodide was added.

The effect of increasing the surface exposed in the reaction tube was rather unexpected. With the tube packed with glass wool, a *decrease* in rate was observed, and the course of the reaction was no longer even approximately unimolecular, as shown by the values of t_{25}, t_{50}, and t_{75} (table 3, previous paper). In the presence of Pyrex rods a similar decrease was noted, but in a lesser degree. The explanation of these results is possibly that of adsorption of iodide or iodine on the surface with reduction in its catalytic activity.

TABLE 2

Time values for experiments with different samples of methyl ethyl ether at various temperatures

SAMPLE OF ETHER	INITIAL PRESSURE	t_{50}			
		at 456-7°C.	at 486-7°C.	at 509-10°C.	at 561-5°C.
	cm.	*minutes*	*minutes*	*minutes*	*minutes*
2	8 and 12			18.9	2.1
3	14 and 17		5.6	2.1	
3	3.2		15.9		
3	15			30.6*	
3	15 and 20		13.5†	7.4†	
4	10.3	29.5			
5	25 to 30	377.6	66.7	34.3	2.2
5	27	9.17 (480°C.)‡			

* In presence of glass wool.

† In presence of Pyrex rods.

‡ Ethyl iodide introduced to a pressure of about 0.06 cm.

The various samples of ether were prepared from the same reagents. The values in table 2 indicate that in ether sample 2 the concentration of iodide was lower than in sample 3. This was to be expected, since in the preparation of sample 2 a smaller proportion of iodide was used in comparison with the sodium methoxide. The chief difference in the method used for sample 5 was in connection with the time allowed. The reaction mixture of methoxide and iodide consists of two layers with the heavy iodide forming the lower. The reaction at the interface is rather slow unless the temperature is raised to such a value that there is danger of the reagent distilling over. In the preparation of sample 5, the mixture was allowed to stand at room temperature until the lower layer had completely disappeared, a matter of six days, after which treatments with sodium and several careful fractionations were carried out. The results seem to point unmistakably to the presence of iodide in the other preparations.

THE KINETICS OF THE CATALYTIC PROCESS

Clusius and Hinshelwood (3) have shown that the decomposition of acetaldehyde catalyzed by iodine follows a unimolecular course with respect to the aldehyde itself, and that the catalytic decomposition of ethyl ether consists of consecutive unimolecular reactions. The same state of affairs is to be expected in the present case, in which a large proportion of the methyl ethyl ether decomposes into acetaldehyde and methane.

The treatment of the experimental results is somewhat simpler than that given for the uncatalyzed process (1). Here a solution of the differential equations is possible, but it is easier to retain the differential form in treating the data.

The value of k_1, the rate constant for the ether, may be obtained as in the previous case or may be estimated from the slope of the pressure–time curve at the origin.

The equation for k_2', the unimolecular constant for acetaldehyde, becomes

$$\frac{\mathrm{d}P}{\mathrm{d}t} = k_1 (P_f - 1.65\, P_i)\, e^{-k_1 t} + k_2' b$$

where as before $\frac{\mathrm{d}P}{\mathrm{d}t}$ is the slope at time t of the curve obtained by plotting the total pressure throughout decomposition against the time. P_f and P_i are the final and the initial pressures respectively, and b is the partial pressure of acetaldehyde at time t.

In table 3 is shown the results of applying this method to an experiment at 480°C., in which 26.95 cm. of ether from sample 5 were used in the presence of ethyl iodide, the pressure due to the catalyst being about 0.06 cm. There is some doubt as to the correct value of k_1, since k_2' is relatively large and the decomposition of the acetaldehyde is taking place at an appreciable rate even at the start. The values of b show the expected rise and fall and values of k_2' for a unimolecular process given in the fourth column show fair agreement up to a time of 20 minutes, after which both b and the pressure of the ether become small. In the last column are shown values calculated for a bimolecular reaction on the part of the acetaldehyde and the variation is much larger than for the unimolecular case. In table 4 the same treatment is applied to an experiment at 456°C. in which 10.25 cm. of ether from preparation 6 was used without further addition of catalyst. Here the agreement in the values of k_2' in column four is quite satisfactory.

As in the uncatalyzed decomposition, the analyses indicate a part of the ether forms formaldehyde and ethane, followed by the rapid decomposition

TABLE 3

Experiment on ether sample 5 and ethyl iodide at 480°C.

$k_1 = 0.146$ min.$^{-1}$

t	P	b	k_2' (uni.)	k_2 (bi.)
minutes	*cm.*	*cm.*		
0	26.95	0		
1	30.15	2.75	0.131	0.048
2	33.15	4.75	0.135	0.028
3	36.05	6.25	0.126	0.020
4	38.85	7.15	0.130	0.018
5	41.45	7.95	0.116	0.015
6	43.85	8.25	0.121	0.015
7	46.15	8.45	0.113	0.013
8	48.05	8.65	0.110	0.013
9	49.9	8.60	0.102	0.012
10	51.5	8.60	0.091	0.011
20	62.3	5.47	0.111	0.020
30	66.7	2.84	0.086	0.030
40	68.5	1.47	0.068	0.046

TABLE 4

Experiment on ether sample 4 at 456°C.

$k_1 = 0.030$ min.$^{-1}$

t	P	b	k_2' (uni.)	k_2 (bi.)
minutes	*cm.*	*cm.*		
0	10.25	0		
10	13.45	1.34	0.034	0.025
20	15.98	2.16	0.029	0.013
30	18.10	2.52	0.025	0.0099
40	19.85	2.60	0.025	0.0096
50	21.25	2.56	0.023	0.0090
60	22.37	2.45	0.022	0.0090
70	23.30	2.27	0.024	0.011
80	24.20	1.92	0.027	0.014
90	24.98	1.55	0.031	0.020
100	25.60	1.23	0.033	0.027
110	26.03	1.03	0.025	0.024
120	26.35	0.87	0.026	0.030
150	27.00	0.51	0.030	0.059
			Av. = 0.027	

of the formaldehyde, and the slow decomposition of a part of the ethane to an equilibrium with ethylene and hydrogen. In the former case the ethane decomposition was found to be relatively slow and heating for a day or two was usually required to reach a constant pressure. Thus in an experiment

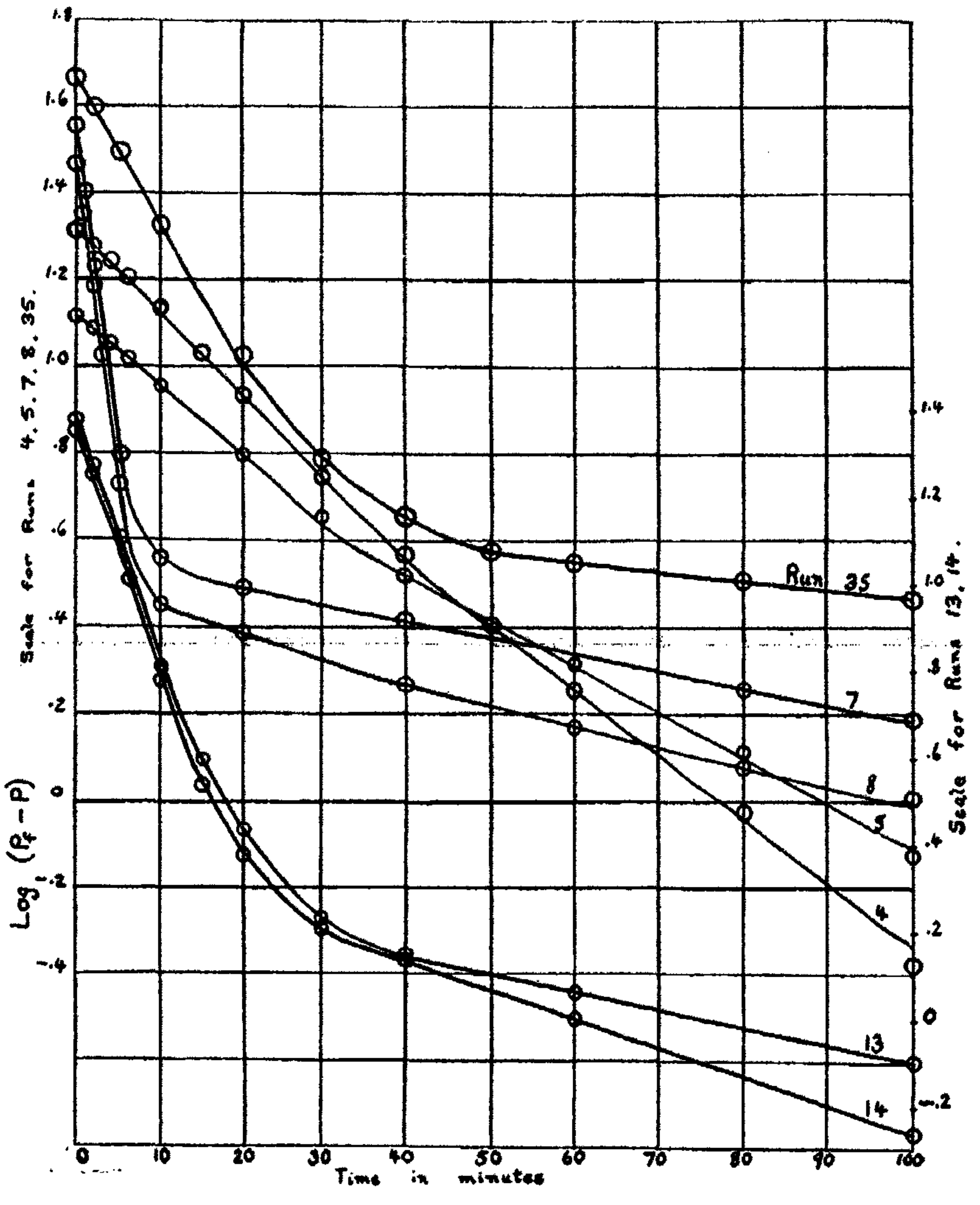

Fig. 1

RUN NO.	TEMPERATURE	INITIAL PRESSURE	ETHER SAMPLE
	degrees C.	*cm.*	
4	503	11.9	2
5	509	7.7	2
7	510	21.0	3
8	510	17.3	3
13	487	14.1	3
14	487	13.4	3
35	480	26.95	5 + ethyl iodide

at 565°C. an approximate calculation based on the pressure rise after 50 minutes gave for a unimolecular constant 3.4×10^{-3} min.$^{-1}$, while from the work of Marek and McCluer (4) the constant for ethane decomposition is calculated to be 8.9×10^{-3} min.$^{-1}$

In the catalytic experiments in most cases there was noted a slow rise in pressure following the first relatively rapid increase. Moreover if a logarithmic plot is made, the lines appear to show two main slopes. This is illustrated in figure 1 in which are plotted the values of log $(P_f - P)$ against the time for a number of the catalytic runs. P is the total pressure at any time, and P_f the final total pressure. If the process was a simple unimolecular one such a plot would produce a straight line. In the figure it is shown that in most cases the lines are approximately straight in the first portion of any run; then there is a rapid change of slope to a much lower value.

The first part of the plot evidently refers to the decomposition of ether followed by that of acetaldehyde, and corresponds approximately to a single unimolecular process, since k_1 and k_2' are close together in value, as shown in tables 3 and 4. That the second slope corresponds to the decomposition of ethane seems a reasonable assumption, since the rate is too slow for that of acetaldehyde, and moreover the amount of pressure change during the second stage is of the right order of magnitude as calculated from the equilibrium data for the reaction

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2 \qquad (5)$$

In the case of runs 4 and 5 (and some others not shown here), the initial rates are slow and the experiments were not carried on long enough to reach the equilibrium pressure.

The experimental data for this final stage in the decomposition process is not sufficiently accurate to provide reliable values of the unimolecular constant for ethane, but approximate calculations indicate considerably higher values than would be expected at the temperatures used. This points to catalysis also in the decomposition of the ethane.

It is to be noted that at the temperatures at which the catalytic reactions were carried out, the uncatalyzed reactions were also taking place at measurable rates, as shown in the previous paper, although in most cases the effect of the latter should be negligible.

SUMMARY

1. The decomposition of methyl ethyl ether is catalyzed in the presence of small quantities of ethyl iodide such as may remain in the ether as a result of its preparation.

2. The catalytic process consists mainly of the unimolecular decompo-

sition of the ether followed by the unimolecular decomposition of the acetaldehyde formed.

3. Ethane seems also to be a primary product and the decomposition to an equilibrium mixture with ethylene and hydrogen is catalyzed as a result of the iodide.

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THE PARTIAL PRESSURES OF WATER IN EQUILIBRIUM WITH AQUEOUS SOLUTIONS OF SULFURIC ACID[1]

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In connection with a method developed by Collins and Menzies for measuring aqueous tensions in salt hydrate systems, which is to be described in a subsequent paper, a knowledge was required of the partial pressures of water over aqueous solutions of sulfuric acid for various concentrations and at various temperatures. Critical discussions of existing data have been given by Wilson (1), Greenewalt (2), and Hepburn (3), and tables have been compiled. The agreement between their values at 25°C. indicates that this isotherm is fairly accurately located. At other temperatures, however, the tables of Wilson and Greenewalt do not agree to the extent expected if the claims of accuracy of each are considered, the disagreement in many cases being more than 4 per cent. We decided, therefore, to redetermine experimentally the vapor pressures over aqueous solutions of sulfuric acid.

CHOICE OF METHOD

The dynamic boiling point method employed by Burt (4) presents many difficulties. Among the principal objections are superheating, change of concentration with boiling, and the existence of a pressure gradient. The gas-current saturation method used by Briggs (5), Sorel (6), and others presents difficulties in temperature control and is accompanied by a change in concentration of the solution. The dew point method used by Hepburn (3) is practical for only moderate temperatures. The static methods used by Regnault (7), Brönsted (8), Dieterici (9), Grollman and Frazer (10), and Hacker (11), permit greater accuracy. A static method was therefore desirable. The method chosen consisted of a modification of the static isoteniscope of Smith and Menzies (12). The partial pressure of hydrogen sulfate or sulfur trioxide over aqueous sulfuric acid solutions is not appreciable below 150°C. According to Thomas and Barker (13) the partial pressure of hydrogen sulfate over a 99 per cent solution is 0.5 mm. at 180°C. Hence a method measuring the total vapor pressure of a solution will, in effect, give results for the aqueous partial pressure.

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[1] From a thesis presented by the author to the Faculty of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

EXPERIMENTAL

Isoteniscope

For details of the static isoteniscope one is referred to the original article (12). The static isoteniscope as described there is applicable in the case of single substances and saturated solutions. It is, however, not directly applicable in measuring vapor pressures of liquid pairs or unsaturated solutions. In these cases the repeated boiling-out to insure the expulsion of all the dissolved or absorbed foreign gases would be followed by a change in the concentration of the solution. It was necessary to devise an isoteniscope which would permit the expulsion of the foreign gases with no accompanying change in concentration. Jacketing the part of the isoteniscope nearest the manometer with a water condenser would prevent loss

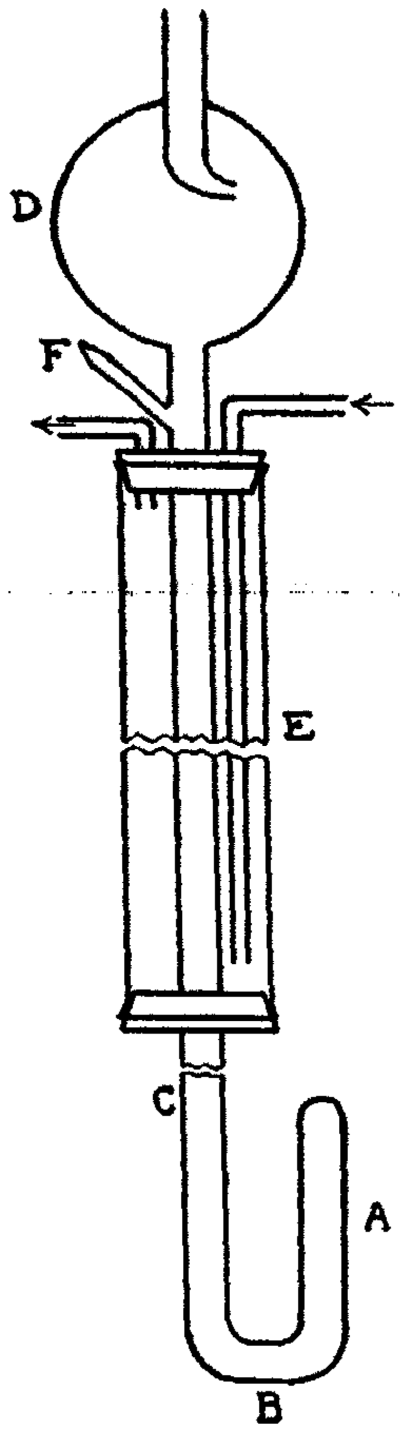

FIG. 1

of water from the instrument itself, but the solution in the bulb would become more concentrated, while the solution acting as the confining liquid would become more dilute on account of the returned condensed water vapor. This difficulty was obviated by abbreviating the instrument to a J-tube (figure 1). It was made from glass tubing (7 mm. internal diameter). The closed end, A, was approximately 6 cm. long and the length over all was 40 cm. The water jacket, E, was constructed from 20-mm. tubing and was fitted to the isoteniscope with rubber stoppers. The condenser was put in place before sealing on the Kjeldahl trap D. It proved convenient to have both the inlet and outlet tubes of the condenser inserted through the top stopper. The Kjeldahl trap was added as a safety device to protect the pressure measuring system from an influx of acid solution should the pressure in the isoteniscope accidentally become much larger than the applied pressure. The side tube, F, which may be opened or sealed at will, permits greater facility in washing and charging.

Since approximately 5 cc. of solution were needed there arose the question of a change in concentration through the possibility of condensed water in part C at times other than during the process of air removal. On no occasion was any water ever observed laving the inner walls of the condenser, so that the amount of water must have been small. And yet no vapor escaped past the condenser, which was proven by the subsequent analysis of several samples of acid solutions after having been used in the pressure determinations from 25°C. to the vicinity of 125°C., the concentration agreeing with the initial concentration within the experimental error. To get an idea how small an amount of water, if any, was on the walls of the condenser the following experiment was performed. The glass tubing between the isoteniscope proper and the condenser was bent so that it was approximately 70° from the vertical and the condenser 20° from the vertical. A piece of glass tubing several centimeters long and having a closed end was sealed to the underside just below the condenser forming an "appendix." The isoteniscope was charged with an acid solution with a boiling point of approximately 110°C. and connected with the pressure measuring system. The isoteniscope proper was maintained at 105°C. and the pressure in the system adjusted accordingly. The "appendix" was kept cold by immersion in a bath of water. At the end of two hours the "appendix" was cut off and its water content determined. The water which collected was inappreciable, i.e., less than 0.01 g., an amount having too small an effect upon the concentration to cause concern. This may not seem surprising when we stop to consider that the only way for the water to reach the condenser was by diffusion through a tube 14 cm. long and of 7 mm. diameter against an opposing equal pressure of air, except during the process of air removal.

Preparation of solutions

The acid solutions used in these determinations were prepared from redistilled sulfuric acid of the best reagent grade. An analysis of the acid was made, which showed that the statement made by the manufacturer regarding the maximum limits of impurities was correct. This statement showed that the acid conformed to the standards of purity as given by Murray (14). The various solutions were analyzed in triplicate for sulfate by precipitating and weighing as barium sulfate. The analyses checked within 0.04 of a percentage of composition, which amounts to an error of less than 0.1 per cent for most of the solutions.

Temperature regulation

For the lower temperatures a water-bath consisting of a 4-liter beaker was used; for the higher temperatures oil was substituted for the water. The bath was jacketed with an inch of asbestos, the variety commonly used for wrapping steam pipes. The temperature was regulated by an electric hot-plate in series with a variable resistance. An additional electric heater of the immersion type was used to facilitate raising the temperature rapidly and then disconnected when the desired temperature was reached. A coil of copper tubing immersed in the bath, through which cold water could be run, afforded the means of cooling when necessary to lower the temperature. The temperature was controlled within 0.01 to 0.02°C. Violent stirring was provided and uniformity of temperature throughout the bath was obtained.

Thermometry

The temperature was measured by means of a platinum resistance thermometer of the Callendar type with compensating leads. The platinum wire was wound on a mica form and was jacketed with a porcelain tube. It was calibrated at the freezing and boiling points of water and at the transition point of sodium sulfate decahydrate.

Resistances were measured by means of a Mueller type thermometer bridge (15). The makers supplied calibration data showing no deviations which would affect our results. The sensitivity of the galvanometer was such that a change in the resistance of the thermometer of 0.001 ohms, corresponding to 0.01°C., produced a deflection of one half a scale division. No thermal E.M.F. causing more than 0.01°C. was observed. The fixed points showed no change throughout the period of the measurements, probably because the thermometer was never heated above 140°C.

Pressure

The manometer was similar to the one described by Smith and Menzies (12). The mercury was purified by the nitric acid treatment and subsequent distillation *in vacuo*. The manometer levels were measured by a graduated steel bar, the length of which was calibrated by comparison with a standard meter, the latter having been calibrated by the late Dr. E. W. Morley. The graduations were compared by means of dividers for 5 cm. intervals. There were no discrepancies large enough to affect our results. The room temperature variation was so small that the bar was not noticeably affected. The steel bar carried a movable sleeve with a vernier scale. To this sleeve was attached a strip of mirrored glass with a horizontal hair line, in such a way that it was behind the manometer tubes on each side of the steel bar. The hair line could be adjusted at the mercury level, avoiding parallax by the alignment of the mercury level with its image. The manometer readings were reduced to millimeters of mercury at 0°C. and to sea level at 45° N.L. The value of the gravity constant, g, was taken as 980.3, the calculated value for Williamstown, Mass., according to its latitude, longitude, and elevation. This value agrees with that determined in the Thompson Physical Laboratory of Williams College.

For pressures less than one atmosphere the "open end" of the manometer was connected to a system containing a Hyvac pump and McLeod gauge. This system was evacuated to a residual pressure of 0.005 mm., thereby obviating the reading of the barometer at each determination and also increasing the accuracy of the measurements.

Pressures less than 10 mm. were read by means of another McLeod gauge protected from water vapor by a guard tube containing magnesium perchlorate trihydrate.

Since an open-end manometer was used for pressures above one atmosphere the barometer had to be read. The barometer was by Henry Green of Brooklyn, N.Y. It was tested for accuracy by comparison with the manometer when the open end was at atmospheric pressure. The Green barometer was found to be accurate within the error of reading the instruments.

Manipulation

The essential difference in the manipulation of this isoteniscope and that of Smith and Menzies was the method by which the dissolved gases were removed. Enough solution was placed in the isoteniscope to fill the closed arm about one-half full when the levels of the solution in both arms were equal. About 5 cc. were required. Then the isoteniscope was connected to the system and the latter evacuated. Bubbles of gas were given off from the solution and part of this gas collected in the closed end of the isoteniscope. This was removed from time to time by bringing the instrument to horizontal position. Sharp tapping aided in the removal of the gas from the solution. After several repetitions of gas removal it was necessary to warm gently the closed end of the instrument in order to form a bubble of water vapor. If the isoteniscope was swung quickly back and forth through a small arc, as a clock pendulum, a sharp click was heard when the solution struck the closed end. This was an index of the absence of foreign gases. As further proof of the removal of gases a measurement of the aqueous tension was made at a given temperature and then the process of gas removal repeated at a higher temperature. A redetermination of the pressure at the first temperature was then repeated and identical values ensured the absence of all foreign gases. Any water which might have deposited in the condenser during the process of air removal was allowed sufficient time to reflux and become thoroughly mixed with the solution before the pressure measurements were made.

EXPERIMENTAL RESULTS

The experimental results are given in table 1.

FINAL TABULATION OF RESULTS

Since the vapor pressures measured were for solutions of various concentrations and at various temperatures it was necessary to devise a method whereby the aqueous tensions of solutions of intermediate concentrations could be obtained at any desired temperature.

The experimental data was first smoothed by a highly sensitive graphical method. In this method the log of the pressure is temporarily assumed to be a linear function of the reciprocal of the absolute temperature. Since log P, however, is not strictly a linear function of $1/T$ there was a difference between the logs of the observed pressures and those so calculated. These differences were plotted as a function of temperature, and by their aid the pressures at rounded temperatures were calculated for intervals of 5°C.

Since the relative vapor pressure for a solution changes only slowly with temperature, graphs showing this relation allowed us to test the data smoothed as above and to smooth it further where necessary. Extrapolation of these curves gave the values for 20°C., 140°C., and in some cases 135°C.

The relative vapor pressures for solutions of rounded concentrations were next obtained graphically. To accomplish this, the logs of the smoothed relative vapor pressures were plotted as a function of the concentration. Although no experimental data was obtained for concentrations below 29.90 per cent the extrapolation of the isotherms from this concentration to 0 per cent was accomplished without the introduction of appreciable error. The logs of the relative vapor pressures for 10 per cent, 20 per cent, and 25 per cent were read directly from these isotherms. Instead of obtaining the logs of the relative vapor pressures for solutions above and including 30 per cent directly from the graphs, we obtained them by a more accurate method. This method involved calculating them on the temporary assumption of a parabolic relation between the log of the relative vapor pres-

TABLE 1

Vapor pressure for sulfuric acid–water solutions

Experimental concentrations. Pressure in millimeters of mercury

t	P (OBSERVED)	t	P (OBSERVED)	t	P (OBSERVED)	t	P (OBSERVED)
29.90 per cent H_2SO_4							
degrees C.		*degrees C.*		*degrees C.*		*degrees C.*	
24.87	17.8	39.69	41.1	69.85	179.0	99.71	590.7
24.41	17.0	44.90	54.5	74.83	221.1	104.44	699.2
30.00	24.1	49.71	69.6	79.67	270.7	110.06	845.1
29.90	23.7	54.91	89.9	85.32	341.9	113.85	964.4
34.45	30.7	59.72	112.9	89.92	408.1	119.33	1155.
34.40	31.0	64.59	141.7	94.78	491.0	123.06	1296.
38.23 per cent H_2SO_4							
25.82	15.0	57.32	82.4	90.67	351.5		
31.44	21.1	63.11	108.4	96.51	440.3		
36.20	27.5	69.69	146.5	103.13	561.1		
45.88	46.3	76.29	195.4	110.80	737.7		
50.51	59.2	82.71	255.4	123.64	1133.		
55.44	74.8	86.09	292.1	129.25	1344.		
43.36 per cent H_2SO_4							
25.20	12.0	54.17	59.2	84.39	231.6	115.56	743.3
29.95	15.6	59.12	75.6	90.16	293.9	119.16	844.9
36.53	23.2	64.75	97.7	94.86	353.1	124.25	996.4
39.99	28.0	69.76	123.7	99.73	423.0		
44.67	36.2	74.79	154.3	104.76	511.9		
49.72	47.0	79.98	193.0	109.92	614.8		
48.12 per cent H_2SO_4							
26.04	10.1	61.60	69.8	94.75	296.1	129.11	990.7
32.81	14.9	69.83	102.4	99.23	349.3		
41.61	24.9	74.53	126.4	104.81	430.3		
46.58	32.4	80.04	160.8	109.64	513.6		
51.18	41.5	84.19	191.8	114.26	602.7		
55.29	51.0	89.41	237.5	121.27	766.1		
52.68 per cent H_2SO_4							
24.49	7.01	54.29	37.9	85.05	159.8	115.53	523.0
29.69	9.60	59.40	49.4	90.29	199.9	119.75	601.2
34.48	13.0	64.57	63.6	94.96	239.8	125.98	750.6
39.93	17.4	70.17	83.4	100.43	298.5		
44.50	22.4	74.42	102.2	105.37	361.2		
50.15	30.7	79.65	127.0	109.20	412.8		

TABLE 1—*Concluded*

t	P (OBSERVED)	t	P (OBSERVED)	t	P (OBSERVED)	t	P (OBSERVED)
58.03 per cent H_2SO_4							
degrees C.		*degrees C.*		*degrees C.*		*degrees C.*	
25.11	4.82	59.95	35.5	89.87	139.5	120.74	453.2
33.95	8.40	65.01	45.6	95.06	172.9	125.42	533.8
40.58	12.4	70.13	58.3	100.15	211.1	130.20	630.0
45.05	16.1	74.95	72.7	104.10	246.2	135.61	752.8
49.77	20.1	80.22	92.2	109.66	303.9		
55.19	28.0	85.16	114.3	114.99	370.1		
65.47 per cent H_2SO_4							
29.72	2.89	59.98	18.02	90.16	77.4	119.13	247.8
34.99	4.29	64.36	22.7	94.71	93.9	124.41	301.2
39.59	5.37	69.86	29.8	100.20	118.5	129.46	361.1
44.66	7.58	74.52	37.6	104.56	141.3		
49.77	10.16	79.19	46.9	109.96	174.9		
54.91	13.74	84.72	60.6	114.74	210.6		

sure and the concentration, a method similar to the one described above where a linear function was temporarily assumed.

Table 2 presents the final tabulation of the relative vapor pressures. The first and second columns, respectively, give the temperature and the vapor pressure of water in millimeters of mercury. The other columns give the relative vapor pressures in per cent for the solutions designated at the head of each column. Values for intermediate concentrations and temperatures may be obtained by linear interpolation from table 2 without introduction of large errors, since the R.V.P. isotherms are sufficiently rectilinear for intervals of 10 per cent and the relative vapor pressure for a solution of given concentration is a linear function of the temperature. Relative vapor pressures at temperatures not far above 140°C. may be obtained by linear extrapolation. Values in table 2 for 145°C. and 150°C. have been so obtained.

ACCURACY OF RESULTS

The maximum absolute error in temperature measurement we estimate at 0.05°C. For our most dilute solution this could cause an error of 0.1 per cent at 125°C. and 1 per cent at 25°C. From a study of the smoothing required of our results we find that the average smoothing required below 10 mm. amounts to 1.5 per cent. Between 10 mm. and 100 mm. the average smoothing amounts to 0.2 per cent. Above 100 mm. it amounts to but 0.1 per cent. In terms of pressure this would correspond to an average better than 0.15 mm. below 10 mm., and 0.2 mm. above 10 mm. This error corresponds to the limit of error in reading the manometer, McLeod gauges, and barometer.

Since the pressures for 10 per cent, 20 per cent, and 25 per cent were obtained by graphic interpolation of the logs of the relative vapor pressures, their accuracy depends upon the accuracy with which the isotherms of log R.V.P. versus concentration were located when they were extrapolated to zero concentration. We estimate that the probable error involved when reading the log of R.V.P. from these isotherms is not more than 0.005 units, which introduces approximately 1 per cent error in the relative and absolute

TABLE 2

Relative vapor pressures for sulfuric acid-water solutions

t	P (FOR WATER)	RELATIVE VAPOR PRESSURES IN PER CENT FOR SOLUTIONS CONTAINING FROM 10 TO 70 PER CENT H_2SO_4											
		10 per cent	20 per cent	25 per cent	30 per cent	35 per cent	40 per cent	45 per cent	50 per cent	55 per cent	60 per cent	65 per cent	70 per cent
degrees C.	*mm.* Hg												
20	17.54	95.6	88.0	82.4	75.0	66.0	56.1	45.6	35.2	25.3	16.1	9.2	3.4
25	23.76	95.6	88.0	82.5	75.2	66.3	56.5	46.1	35.7	25.8	16.6	9.7	3.7
30	31.82	95.6	88.0	82.6	75.4	66.6	56.9	46.6	36.2	26.3	17.1	10.1	4.1
35	42.18	95.6	88.1	82.8	75.6	66.9	57.3	47.1	36.8	26.8	17.5	10.5	4.4
40	55.32	95.6	88.1	82.9	75.8	67.3	57.7	47.5	37.3	27.4	18.0	11.0	4.7
45	71.88	95.6	88.2	83.0	76.0	67.6	58.1	48.0	37.8	27.9	18.5	11.4	5.1
50	92.51	95.6	88.2	83.1	76.2	67.9	58.5	48.5	38.3	28.5	19.0	11.8	5.4
55	118.0	95.6	88.3	83.2	76.4	68.2	58.9	48.9	38.9	29.0	19.5	12.3	5.8
60	149.4	95.6	88.3	83.3	76.6	68.5	59.3	49.4	39.4	29.6	20.0	12.7	6.2
65	187.5	95.6	88.4	83.4	76.8	68.8	59.7	49.9	39.9	30.1	20.4	13.1	6.5
70	233.7	95.6	88.4	83.5	77.0	69.1	60.1	50.4	40.5	30.6	20.9	13.5	6.8
75	289.1	95.6	88.5	83.6	77.2	69.5	60.5	50.8	41.0	31.1	21.4	14.0	7.2
80	355.1	95.6	88.5	83.8	77.4	69.8	60.9	51.3	41.5	31.7	21.9	14.4	7.5
85	433.6	95.6	88.6	83.9	77.6	70.1	61.3	51.7	42.1	32.2	22.4	14.8	7.8
90	525.8	95.6	88.6	84.0	77.8	70.4	61.7	52.2	42.6	32.7	22.8	15.2	8.2
95	633.9	95.6	88.7	84.1	78.0	70.7	62.2	52.7	43.1	33.2	23.3	15.7	8.5
100	760.0	95.6	88.7	84.2	78.2	71.0	62.6	53.1	43.6	33.8	23.8	16.1	8.9
105	906.1	95.6	88.8	84.3	78.4	71.3	63.1	53.6	44.2	34.3	24.3	16.5	9.3
110	1075.	95.6	88.8	84.4	78.6	71.7	63.4	54.1	44.7	34.9	24.8	17.0	9.6
115	1268.	95.6	88.8	84.6	78.8	72.0	63.8	54.5	45.2	35.4	25.2	17.4	9.9
120	1489.	95.6	88.9	84.7	79.0	72.3	64.2	55.0	45.7	35.9	25.7	17.8	10.2
125	1741.	95.6	88.9	84.8	79.2	72.6	64.6	55.5	46.3	36.5	26.2	18.3	10.6
130	2026.	95.6	89.0	84.9	79.4	72.9	65.0	55.9	46.8	37.0	26.7	18.7	11.0
135	2347.	95.6	89.0	85.0	79.6	73.2	65.4	56.4	47.3	37.6	27.1	19.1	11.3
140	2710.	95.6	89.1	85.1	79.8	73.5	65.8	56.8	47.8	38.1	27.6	19.5	11.7
145	3117.	95.6	89.1	85.2	80.0	73.8	66.2	57.3	48.3	38.6	28.1	19.9	12.0
150	3570.	95.6	89.2	85.3	80.2	74.1	66.6	57.8	48.8	39.1	28.6	20.4	12.4

vapor pressures. For the concentrations from 30 per cent to 65 per cent whose relative vapor pressures were obtained as described, the probable error is not more than 0.3 per cent. Since the pressures for 70 per cent were obtained by extrapolation, their accuracy is probably not better than 1 per cent.

Table 3 compares our values at 25°C. with those of Hepburn, Wilson, and Greenewalt. A comparison with the values of Wilson and Greenewalt at higher temperatures seems to show better agreement between our values and those of Greenewalt, although in many instances our values are intermediate between those of Wilson and Greenewalt.

TABLE 3

Comparative 25° isotherm

Rounded concentrations. Pressures in millimeters of mercury

SULFURIC ACID	OUR VALUES	VALUES OF WILSON	VALUES OF GREENEWALT	VALUES OF HEPBURN
per cent				
10	22.7	22.8	22.4	22.7*
20	20.9	21.0	20.8	20.9*
25	19.6	19.7	19.4	19.6*
30	17.9	17.9	17.8	17.8
35	15.8	15.8	15.8	15.8
40	13.4	13.5	13.5	13.4
45	11.0	11.1	10.9	10.9
50	8.48	8.7	8.45	8.36
55	6.13	6.3	6.15	6.05
60	3.94	4.1	3.97	3.95
65	2.30	2.3	2.24	2.14
70	0.88	1.2	1.03	0.88
75		0.55	0.41	0.41
80		0.19	0.12	0.13

* Agree with the values obtained from the data of Grollman and Frazer (10).

RELATED THERMAL DATA

The heat of vaporization of water from an aqueous solution of sulfuric acid may be calculated from our vapor pressure data by the aid of the Clausius-Clapeyron equation in its approximate form

$$\frac{d \ln P}{dT} = \frac{Q}{RT^2} \qquad (1)$$

Here Q is the heat absorbed in the evaporation of one mole of water from a large amount of solution so that there is no accompanying change in concentration. This is equal to the heat effects involved in removing one mole of liquid water from the solution and evaporating it. If we assume Q to be constant, we may integrate and obtain the equation:

$$\log P = -\frac{Q}{2.3\,RT} + B \qquad (2)$$

Upon plotting log P versus $1/T$ we obtain a line whose slope is $\frac{Q}{2.3R}$. The heat of vaporization, however, and in consequence the slope, is known to decrease with increasing temperature, attaining the value zero at the critical temperature.

The graphs of our results showed that the slopes of these curves were functions of the concentration as well as the temperature. The slope and the heat of vaporization increase with the concentration of sulfuric acid, since more work is required to remove water from a solution of greater concentration (cf. Greenewalt 2). The heat of vaporization at a given temperature could be calculated from the slope at that temperature. Since, however, the slope changes with temperature, it is best that there be chosen a small temperature interval to obtain the slope from the ratio $\frac{\Delta \log P}{\Delta 1/T}$. The values of $\Delta \log P$ and $\Delta 1/T$, however, can be made necessarily small only at the sacrifice of the accuracy of the ratio.

TABLE 4

Heats of vaporization for sulfuric acid-water solutions

Q (calories per gram) = A t°C. + B

	WATER	10 PER CENT	20 PER CENT	25 PER CENT	30 PER CENT	35 PER CENT	40 PER CENT	45 PER CENT	50 PER CENT	55 PER CENT	60 PER CENT	65 PER CENT	70 PER CENT
A........	−.61	−.61	−.61	−.61	−.61	−.61	−.61	−.61	−.61	−.61	−.61	−.68	−.95
B........	597	597	599	601	604	610	618	626	634	644	655	690	754

In order to avoid this difficulty the method of calculating the heats of vaporization was modified. Since Q is a function of the rate of change of log P with $1/T$ it follows that for two substances the ratio of the heats of vaporization at a given temperature is equal to the ratio of their rates of change of log P at that temperature. Furthermore, the interval determining the rate of change of log P need not be necessarily small. This is shown as follows: For the first substance

$$Q_1 = \frac{2.3\ RT^2\ d\log P_1}{dT}$$

and for the second substance

$$Q_2 = \frac{2.3\ RT^2\ d\log P_2}{dT}$$

Then at the same temperature the ratio of the heats of vaporization

$$\frac{Q_1}{Q_2} = \frac{2.3\ RT^2\ \mathrm{d}\log P_1}{2.3\ RT^2\ \mathrm{d}\log P_2} = \frac{\mathrm{d}\log P_1}{\mathrm{d}\log P_2} = \frac{\Delta\log P_1}{\Delta\log P_2}$$

By substituting the values for water for Q_2 and $\Delta\log P_2$ obtained from the International Critical Tables and our data for $\Delta\log P_1$ for intervals of 5°C. we calculated the heats of vaporization of water from the acid solutions. The values so obtained were next smoothed by plotting them as a function of the temperature. In drawing these curves it was borne in mind that the heat of vaporization for a solution must decrease at a rate not less than that for water. If this were not so the log P versus $1/T$ curve for a solution would intersect that for water at some temperature. Our smoothed heats were found to be represented by a linear equation whose constants are given in table 4. By means of this equation the heats of vaporization at a certain temperature may be calculated with an accuracy of approximately 1 per cent. Upon calculating the heats of vaporization from Greenewalt's table we concluded that his table was not sufficiently accurate to show the required decrease with temperature.

SUMMARY

A redetermination of the aqueous partial pressures over aqueous sulfuric acid solutions has been made for concentrations up to 70 per cent H_2SO_4 from 20°C. to 140°C. For this purpose an isoteniscope was devised which could measure vapor pressures of solutions with no accompanying change in the concentration of the solution. From the observed data a table of relative vapor pressures has been compiled, from which table it is possible to ascertain the aqueous partial pressure for aqueous solutions of sulfuric acid between 0 per cent and 70 per cent H_2SO_4 for any temperature from 20°C. to 140°C. inclusive. The heats of vaporization of water from solutions of the above range of concentration and temperature have been calculated and tabulated.

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THE EFFECT OF DISSOLVED ELECTROLYTES ON THE BOUNDARY TENSION OF WATER

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It is often difficult to employ the capillary rise method for the determination of the interfacial tension of liquid–liquid interfaces. As a result of the work of Lohnstein (1) and of Harkins (2) on the modification of Tate's law, the drop volume method is probably the most precise and universally applicable substitute for use with this type of system.

When the drop volume method is used, the drops must form under as nearly equilibrium conditions as possible. This makes it necessary that the drops form entirely without outside assistance and that they form slowly, the maximum rate of drop formation depending on the time necessary for the attainment of interfacial equilibrium.

The purpose of the present study was to devise an apparatus for the convenient and accurate measurement of the interfacial tension of liquid–liquid systems, and to investigate the effect produced on the interfacial tension of such systems by various concentrations of the salts of the lower fatty acids. It was hoped that such measurements might throw some light on the boundary effects of strong electrolytes in solution.

APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus, a diagram of which is shown in figure 1, was constructed of Pyrex glass. It consists of a storage reservoir (R), from which either phase may be transferred either to the pipette (P) or to the flask into which the drops fall. The pipette is connected by a length of capillary tubing to the carefully ground glass dropping tip (T) by means of a ground glass joint. The tip was machined in a lathe and the dropping surface was made perfectly plane and perpendicular to the sides. The plane surface of the tip was roughened to insure complete wetting by the dropping liquid. The reservoir, pipette, and dropping flask were all connected so that a closed, isobaric system resulted. All connections were made by means of greaseless stopcocks and ground glass joints. By means of a threaded adjustment (A) attached to the top of the Pyrex needle valve (V), the speed of flow could be easily and reproducibly controlled.

The drops were caused to fall between two platinum electrodes (E) immersed in the oil phase. These electrodes were connected in series with a 1000-cycle tuning fork oscillator and the input of a vacuum tube amplifier using a UX280 rectifying tube and a UX210 amplifying tube. A diagram of the apparatus is shown in figure 2. The output leads from the amplifier were connected to the primary winding of a transformer, the ratio of which was 1600 to 1. The secondary winding of this transformer was connected in series with a specially constructed hot wire galvanometer (figure 3).

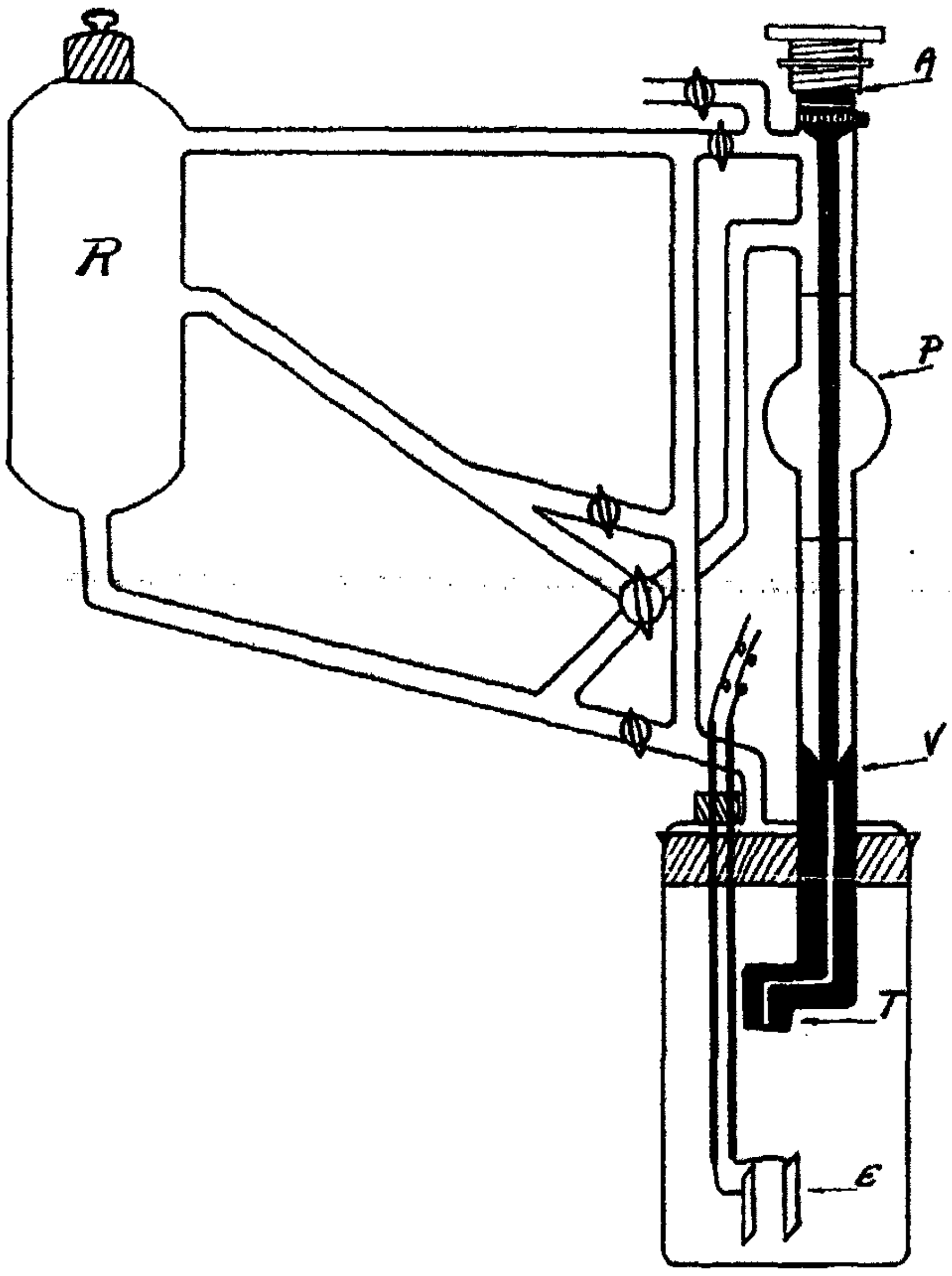

FIG. 1. DIAGRAM OF INTERFACIAL TENSION APPARATUS

The galvanometer consisted of a length of No. 40 B & S gauge iron wire (W), one end of which was attached to a binding post and the other near the center of the balance wheel of an alarm clock. The clock framework was attached to the wooden support by means of flat steel springs (S). In order to relieve the small wire of the necessity of maintaining the tension between the clock framework and the support, and also in order to provide a compensator for variations in room temperature, a length of No. 20 gauge iron wire (C) was used. An aluminum wire (P) bearing a parchment paper pointer and a counterbalance (B) was attached to the balance wheel. The pointer serves as a marker on the slowly revolving smoked drum of a kymograph (K). The operation of the recording device depends on the heating effect of the amperage flux in the galvanometer circuit resulting from the passage of the drop of the aqueous solution between the electrodes.

The apparatus, with the exception of the recording device, was contained in a large, well-insulated air bath, the temperature of which was maintained at 40.00° ± 0.05°C. The air was stirred by means of an 8-inch fan which was suspended from springs supported from without the bath. Vibration was further reduced by placing the bath on a rubber foundation.

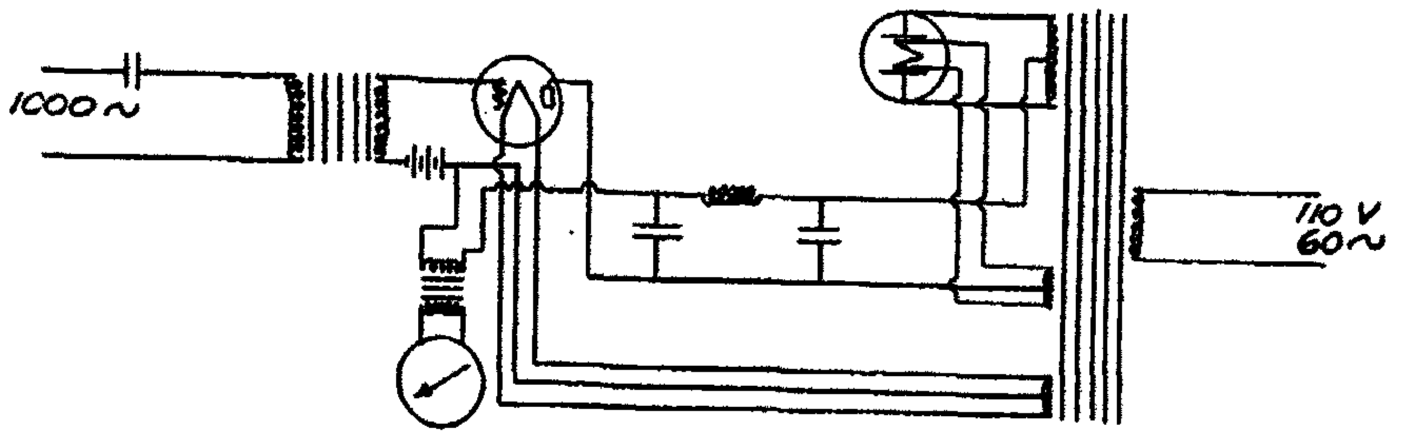

Fig. 2. Wiring Diagram of Amplifier

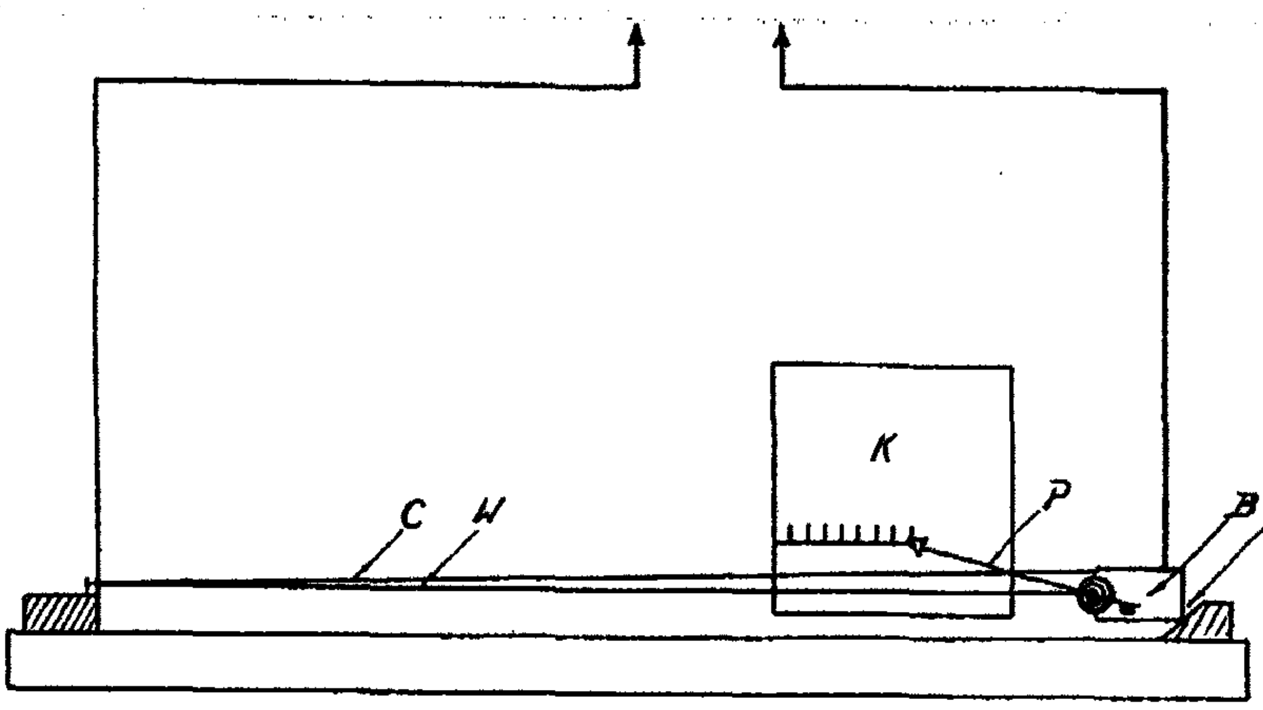

Fig. 3. Diagram of Recording Device

The dropping pipette was carefully calibrated with both mercury and water at 40.00°C. The volume of the bulb between the calibration marks was found to be 21.1106 cc. The volume of the tube near the upper calibration mark was 0.3632 cc. per centimeter length, while the volume of the tube near the lower calibration mark was 0.3605 cc. per centimeter length. The height of the meniscus was read to 0.01 cm. by means of a cathetometer. The probable error in total volume is, therefore, of the order of

0.01 per cent. The diameter of the tip, measured by means of a precision micrometer, was 0.7042 cm.

When making a measurement of interfacial tension the two liquids were first thoroughly mixed at 40.00°C. and placed in the reservoir. From the reservoir the aqueous phase was transferred to the pipette and the oil phase to the dropping flask. The volume of liquid which flowed through the dropping tip was determined by reading the height of the meniscus immediately following the fall of the drop just preceding the first drop counted, and following the last drop counted. The needle valve was not adjusted after a run was once started.

The densities of the mutually saturated phases were determined at 40.00°C., using Ostwald type pyknometers with ground glass caps.

Mineral oil and toluene were used as the oil phases. The mineral oil was a good quality of medicinal oil. The toluene was washed with sulfuric acid and sodium hydroxide and was fractionally distilled. Only the middle fraction of the distillate, boiling between 109.8°C. and 109.9°C. at 748 mm., was used.

The salts were carefully purified by repeated recrystallization from conductivity water. Conductivity water was used in making up all aqueous phases.

RESULTS

The interfacial tensions were calculated by use of the Harkins modification of the equation of Tate,

$$\gamma = \frac{V(d_2 - d_1)\, g\, \Phi}{2\,\pi\, r}$$

in which V is the volume of the falling drop obtained by dividing the total volume of liquid by the number of drops, d_2 and d_1 are the densities of the aqueous and oil phases respectively, g is the gravitational constant, and r is the radius of the tip. Φ is the reciprocal of the Ψ function of Harkins which is the fraction of the pendant drop which falls from the tip. The values of Φ were read from a large graph of the data of Harkins (3) where Φ is plotted against $r/V^{1/3}$.

The data are tabulated in tables 1 to 4, and are shown graphically in figures 4 and 5.

The interfacial tension of mineral oil–sodium acetate systems decreases hyperbolically with increasing sodium acetate concentration from zero to 6 molal. Sodium formate, however, affects the interfacial tension quite differently in that there is a distinct minimum in the interfacial tension–concentration curve. At high concentrations of sodium formate the interfacial tension is greater than at zero concentration.

The interfacial tensions between sodium formate solutions and toluene

TABLE 1

The interfacial tensions of aqueous sodium acetate-mineral oil systems at 40.00°C.

SALT CONCENTRATION	DROP VOLUME	DENSITY AQUEOUS PHASE	DENSITY OIL PHASE	Φ	γ
molal	*cc.*				*dynes per cm.*
0.00	0.50779	0.99222	0.83892	1.4928	51.52
0.05	0.48752	0.99454	0.83901	1.4972	50.34
0.10	0.45833	0.99607	0.83905	1.5060	48.05
2.04	0.28063	1.07150	0.83902	1.5600	45.14
6.12	0.18354	1.16845	0.83903	1.6090	43.13

TABLE 2

The interfacial tensions of aqueous sodium formate-mineral oil systems at 40.00°C.

SALT CONCENTRATION	DROP VOLUME	DENSITY AQUEOUS PHASE	DENSITY OIL PHASE	Φ	γ
molal	*cc.*				*dynes per cm.*
0.00	0.50779	0.99222	0.83892	1.4928	51.52
0.15	0.47054	0.99860	0.83904	1.5010	49.98
0.75	0.40181	1.02224	0.83902	1.5185	49.56
4.11	0.24295	1.12932	0.83902	1.5775	49.33
9.22	0.17435	1.24922	0.83906	1.6145	51.20

TABLE 3

The interfacial tensions of aqueous sodium acetate-toluene systems at 40.00°C.

SALT CONCENTRATION	DROP VOLUME	DENSITY AQUEOUS PHASE	DENSITY OIL PHASE	Φ	γ
molal	*cc.*				*dynes per cm.*
0.00	0.34863	0.99064	0.84027	1.5345	35.67[*]
0.10	0.30629	0.99866	0.84020	1.5515	33.39
1.02	0.27007	1.03382	0.84025	1.5645	36.27
2.04	0.22366	1.07325	0.84023	1.5871	36.68

[*] Value listed in International Critical Tables = 35.7.

TABLE 4

The interfacial tensions of aqueous sodium formate-toluene systems at 40.00°C.

SALT CONCENTRATION	DROP VOLUME	DENSITY AQUEOUS PHASE	DENSITY OIL PHASE	Φ	γ
molal	*cc.*				*dynes per cm.*
0.00	0.34863	0.99064	0.84027	1.5345	35.67
0.75	0.27827	1.01315	0.84020	1.5605	33.31
3.00	0.19208	1.09135	0.84020	1.5800	33.80
9.22	0.11629	1.28660	0.84025	1.6483	37.94

when plotted against the concentration of the salt give a curve of the same type as that obtained when mineral oil was used as the oil phase. Against toluene the sodium acetate solutions also yielded an interfacial tension curve which passes through a very abrupt minimum.

The only value listed which may be strictly compared with accepted values is that of toluene against water. The International Critical Tables list the interfacial tension of this system at 40.00°C. as 35.7 dynes per centimeter, while three consecutive determinations with the apparatus described yielded values of 35.66, 35.67, and 35.67 dynes per centimeter.

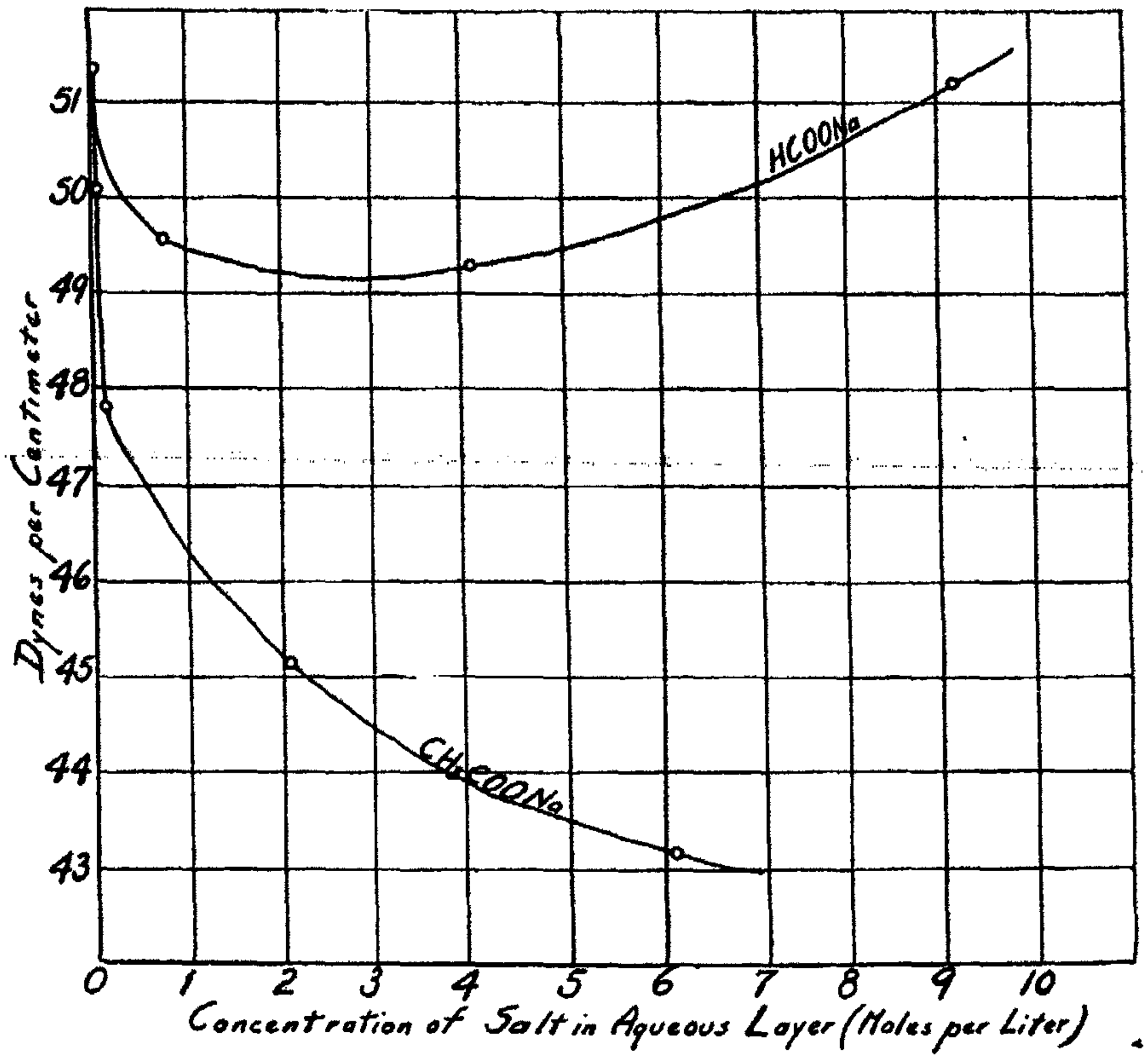

FIG. 4. THE EFFECT OF SODIUM ACETATE AND SODIUM FORMATE ON THE INTERFACIAL TENSION OF WATER-MINERAL OIL SYSTEMS

DISCUSSION

The lowering of the interfacial tension of water-oil systems by low concentrations of salts of the lower fatty acids is to be expected, but the striking effect of high concentrations of these salts in raising the interfacial tension is a phenomenon which apparently has not been observed by previous workers. This type of behavior cannot be satisfactorily explained without some modification of the present theories of the surface effect of solutes. The results of Traxler and Pittman (3), which show exactly the same effect for sodium chloride on the interfacial tension of water–asphalt systems, suggest that the correct explanation will be based on the electrical forces acting between ions in the interface.

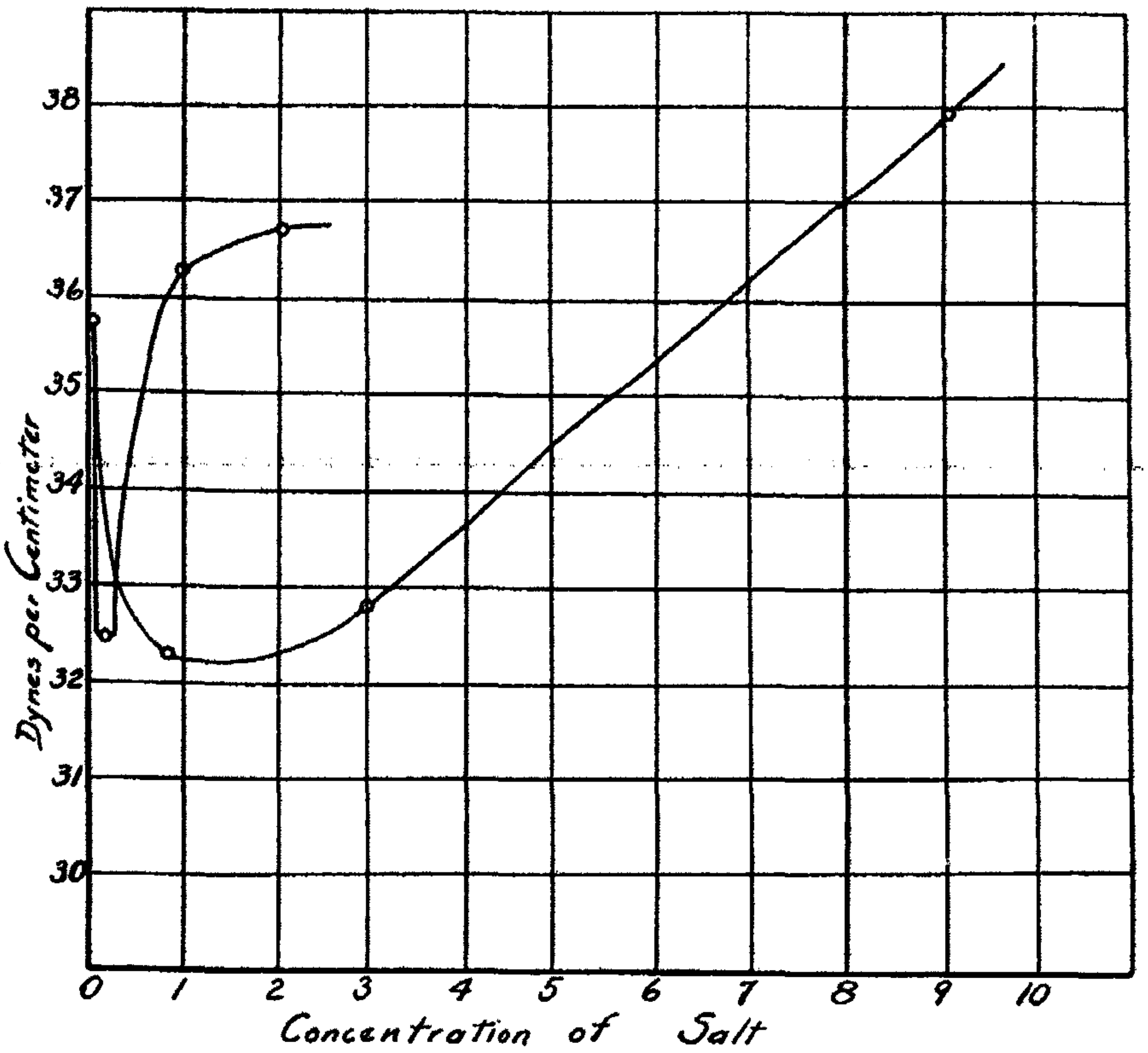

FIG. 5. THE EFFECT OF SODIUM ACETATE AND SODIUM FORMATE ON THE INTERFACIAL TENSION OF WATER–TOLUENE SYSTEMS

van der Waals in his accepted theory of surface tension at the liquid–vapor interface makes the assumption that the liquid and vapor phases are separated by a boundary layer of finite thickness in which the properties change gradually from those of the pure liquid on one side to those of the vapor on the other side. We may assume a similar boundary layer between two immiscible or partially miscible liquids. In this case, the two phases are the mutually saturated solutions, and the properties such as composition, density, and dielectric constant gradually change through an interfacial layer of finite thickness from those of one phase to those of the other.

According to the accepted theories of the surface effects of solutes, fatty acids or their ions orient themselves in the interfacial layer. Thus the acetate ions become concentrated in the interfacial layer, the hydrocarbon end tending to turn toward the oil and the carboxyl group toward the water. However, the exact location of the ions in the interfacial layer is determined as the resultant of three forces. The attraction of the oil phase for the hydrocarbon end of the ion tends to pull it up into the oil-like portion of the boundary layer. This force is opposed by the attraction of the water phase for the carboxyl end of the ion and by the electrostatic attraction of the sodium ion, which is hydrophilic and tends to remain in the water phase. Under a given set of conditions the acetate ions assume a certain equilibrium level in the interfacial layer, depending upon the equality of the opposing forces. Decreasing the concentration of the salt in the water phase increases the attraction of the water phase for the carboxyl group and shifts the equilibrium position toward the water-like side of the interfacial layer. On the other hand, increasing the concentration of salt decreases the attraction of the water phase for the carboxyl end of the ion, and the equilibrium position shifts toward the oil-like side of the interface.

The acetate ions and other fatty acid ions exert two opposing effects on the interfacial tension. By concentrating in the interface they decrease the attraction of the surface layer elements for each other and thus tend to decrease the interfacial tension as do the corresponding free fatty acids. On the other hand, oriented negative ions held at a certain equilibrium level in the boundary layer attract sodium or other positive ions into the boundary layer. The sodium ions occupy positions a little nearer the water side of the interface, each sodium ion occupying a mean position equidistant from two or more acetate ions. This effect gives rise to an increased attraction between the surface layer elements and, therefore, to an increased interfacial tension.

At low salt concentrations, the tension lowering effect predominates because, as pointed out above, the equilibrium position of the acetate ion is shifted toward the water side of the interface where the dielectric constant is high and the attraction between oppositely charged ions is correspondingly small. Furthermore, much of the effect at low salt concentrations may be due to free acid formed by hydrolysis. Undissociated free acid would have no tendency to raise the interfacial tension.

At high salt concentrations the acetate ions are shifted toward the oil-like side of the boundary layer. In this region, owing to the much lower dielectric constant, the attraction between the oppositely charged ions becomes much greater. For this reason, the tendency of fatty acid ions to increase the interfacial tension is greater at high concentration, and it may become even greater than the lowering effect, resulting in a system which has a higher interfacial tension than at zero salt concentration. Interfacial tension is defined as the work done in creating one square centimeter of fresh interface. It is evident that more work would be necessary if there were more closely attracted ions in the boundary layer.

On the basis of this hypothesis, the interfacial tension–concentration curves for sodium acetate and sodium formate would be expected to cross. At low concentrations the interfacial tension lowering should be greater for the acetate than for the formate, owing to the fact that the surface activity of the fatty acids increases with increasing molecular weight. At higher concentrations where the tendency of the ions to increase the interfacial tension becomes an important factor, the attraction of the oil phase for the hydrocarbon end of the ion would be greater for the acetate ion than for the formate ion. At equal surface concentrations, therefore, the equilibrium position of the acetate ion would be nearer the oil side of the boundary layer. This would lead to a greater increase in the interfacial tension of the acetate solution. Owing to the fact that the acetate ions are more highly adsorbed in the interface than the formate ions, the tendency of the sodium acetate to increase the boundary tension would be expected to appear at a lower total salt concentration.

The effect of most strong electrolytes in increasing the surface tension of water may be due to a similar type of effect. The less hydrophilic ion, or the ion which has the greater escaping tendency from the aqueous phase, would occupy a position in the boundary layer somewhat nearer the non-aqueous phase than would the more hydrophilic ion, the equilibrium position of both ions shifting toward the non-aqueous phase with increasing electrolyte concentration in the aqueous phase. Thus the same electrical forces which have been postulated in the case of the sodium acetate and sodium formate solutions would be set up in the boundary layer separating any aqueous solution of a strong electrolyte from a non-aqueous phase in which the electrolyte is practically insoluble. Under such conditions the tension raising effect of the electrolyte should increase with increasing concentration of electrolyte and with increasing difference between the hydrophilic properties of the two ions.

SUMMARY

By means of a specially designed apparatus the drop volume method of measuring interfacial tensions has been employed to yield very accurate results.

The effect of sodium acetate and of sodium formate on the interfacial tension of oil-water systems is very different from that of the free acids.

An attempt to explain the effect of these salts has been made on the basis of the Langmuir theory of molecular orientation and the increased interionic attraction in the interface due to the dielectric constant gradient in the interfacial layer.

The effect of strong electrolytes in general on boundary tension may be explained in a similar manner.

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THE EFFECT OF SODIUM ACETATE ON THE INTERFACIAL TENSION OF THE BENZENE-WATER SYSTEM AT 40°C.

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A great deal of study has been made of organic liquid-aqueous solution interfaces by Reynolds (1), Harkins (2), Morgan (3), and others. In a recent publication by Eversole and Dedrick (4) it is shown that the sodium salts of formic and acetic acids affect the interfacial tension of water-oil systems in a rather unexpected way. It is shown that when the interfacial tension of the system is plotted against the concentration of the solute in the aqueous phase the curve obtained passes through a minimum and that at higher concentrations the interfacial tension is greater than at zero concentration.

The purpose of the present investigation was to extend the previous work (4) to other systems in an attempt to ascertain whether or not the effects noted in it are general.

APPARATUS AND MATERIALS

The apparatus is essentially that used in the work described above (4) except that it has been much simplified and that refinements have been made in the drop counting device. The diagram of the apparatus is shown in figure 1. It consists of a storage reservoir (R) from which the aqueous phase is transferred to the pipette (P) by suction. From the pipette, the solution passes through a needle valve (V) to the tip (T) from which it drops while at equilibrium with the oil phase contained in the dropping flask (F). The speed of flow was controlled by the screw adjustment (A) attached to the top of the needle valve. The dropping tip was ground perfectly flat and perpendicular to the bore of the tube, after which the surface was roughened slightly to insure complete wetting by the liquid phase dropping from it. The tip is removable and is connected to the pipette by a ground glass joint (S). Greaseless stopcocks and ground glass joints were used in all parts of the system.

The apparatus is mounted in a constant temperature air bath which was kept at 40.00° ± 0.05°C. All adjustments were made and the pipette refilled from outside the bath so that duplicate runs were made without the necessity of opening the thermostat.

The drop counting device is based on the same principle as that used in the previous work (4). An improved amplifier and a standard Fries weather recording device (figure 2) were used. With this apparatus a continuous twenty-four hour inked record could be made without attention from the operator. The current for operating the recording device is controlled by a sensitive relay which is connected in the plate circuit of the amplifying tubes.

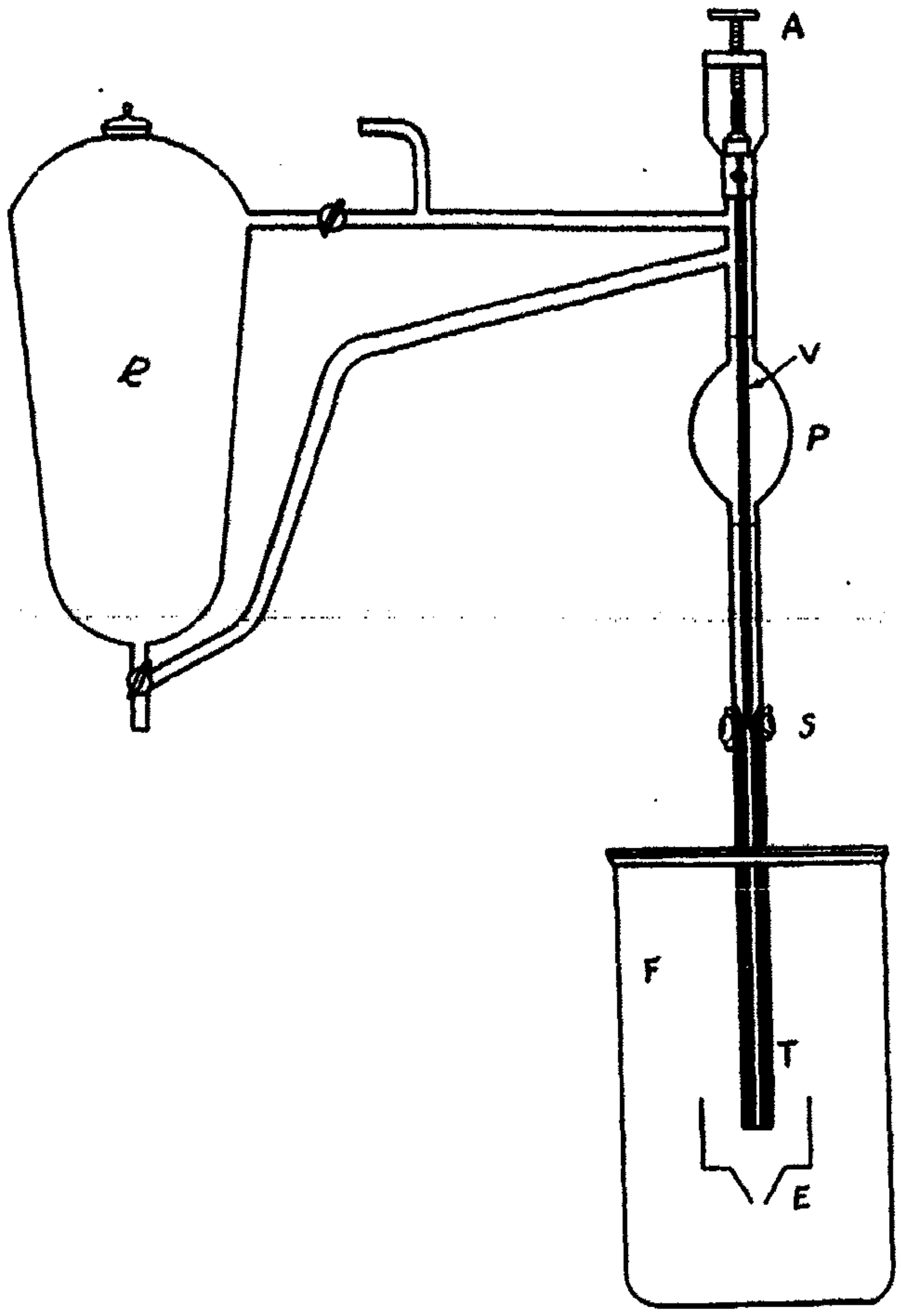

FIG. 1. DIAGRAM OF INTERFACIAL TENSION APPARATUS

The diameter of the dropping tip was carefully measured with a micrometer and found to be 0.9156 cm. The volumes of the pipette between the calibration marks and of unit length of the tubing above and below the calibration marks were determined at 40°C. with mercury and with water. The level of the meniscus was read to 0.01 cm. by means of a cathetometer which was placed outside the thermostat. Using the results of several measurements, all possible combinations of two simultaneous equations of the following form

$$l\frac{dV}{dl} + V_b = V_t$$

were solved for the values of V_b and dV/dl. In the above equation, l is the distance between the initial and final heights of the meniscus minus the distance between the calibration marks, dV/dl is the volume per unit length of tube near the calibration marks, V_b is the volume of the pipette between the calibration marks, and V_t is the total volume of liquid run out during the calibration. The total volume was determined from the weight and density of the liquid. The error in total volume is probably less than 0.01 per cent.

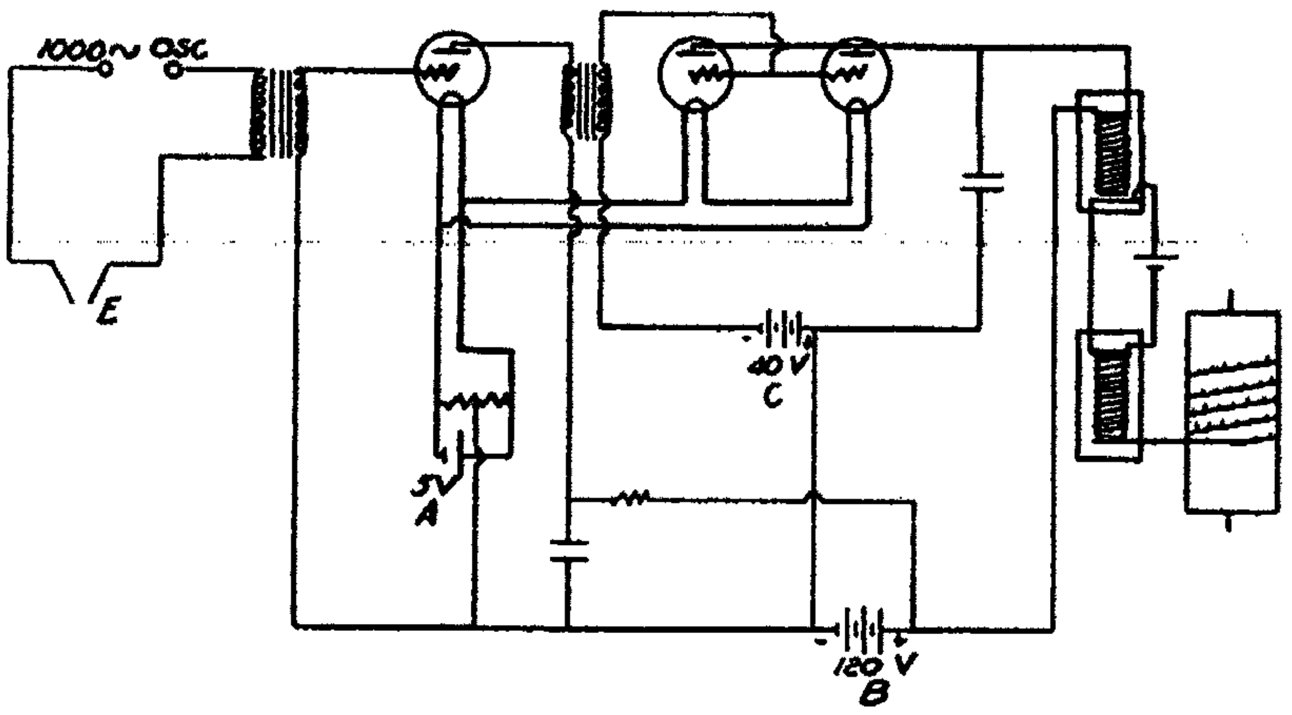

FIG. 2. DIAGRAM OF AMPLIFIER AND RECORDING DEVICE

The benzene was of standard quality and free from thiophene. Only the middle fraction boiling at 79.8°C. at a pressure of 741 mm. was used. The sodium acetate was Baker's analyzed product which had been twice recrystallized from conductivity water. All solutions were made using conductivity water as a solvent.

RESULTS

Experimental measurements and calculations were carried out in the manner described in the previous paper (4). Experimental results are given in table 1 and shown graphically in figure 3.

At very low concentrations the interfacial tension of benzene–sodium acetate systems decreases markedly with increasing concentration of the salt. After passing through a decided minimum at about 0.1 molal, the interfacial tension increases quite abruptly with a small increase in concentration. It then passes through a maximum, the value of which is

TABLE 1

The effect of sodium acetate on the interfacial tension of the benzene–water system at 40°C.

SALT CONCENTRATION	DROP VOLUME	$d_2 - d_1$	Φ	γ
molal	*cc.*			*dynes per cm.*
0.0000	0.46263	0.13342	1.5967	33.85
0.1458	0.42956	0.13968	1.6036	32.80
1.0555	0.38010	0.16419	1.6129	34.32
2.3505	0.31431	0.20415	1.6324	35.71
3.6572	0.25835	0.24465	1.6485	35.52
4.1074	0.24614	0.24540	1.6523	34.02
5.4112	0.21195	0.27915	1.6608	33.50
7.1167	0.17047	0.33667	1.6680	32.64

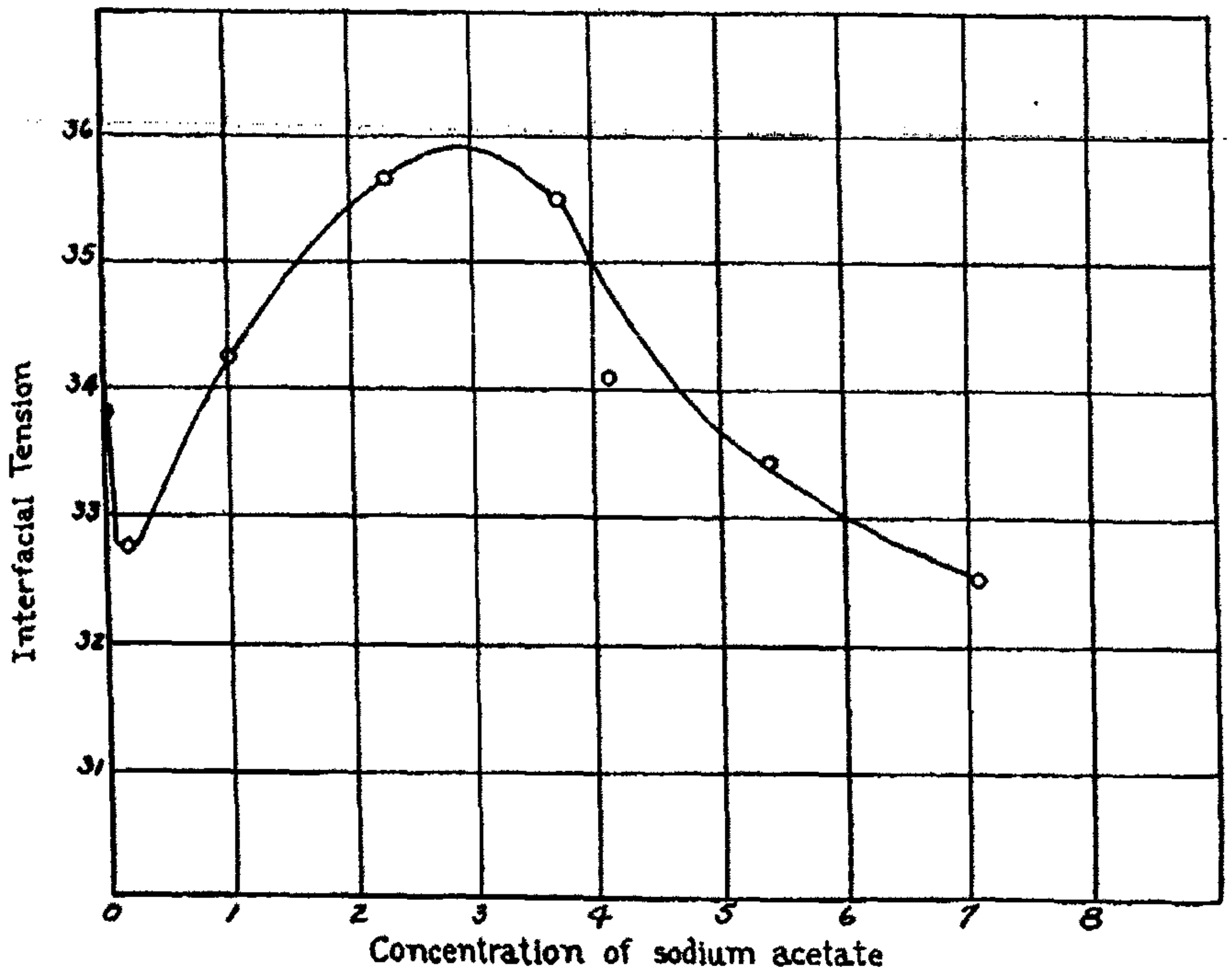

FIG. 3. THE EFFECT OF SODIUM ACETATE ON THE INTERFACIAL TENSION OF WATER–BENZENE SYSTEMS

greater than the initial tension between benzene and water. It then decreases hyperbolically as the solution becomes more nearly saturated.

The only value obtained which may be strictly compared with accepted values is that of benzene against water. The value listed in the International Critical Tables for this system at 40°C. is 33.84 dynes per centimeter. The data presented herewith show the interfacial tension of this system to be 33.85 dynes per centimeter.

DISCUSSION

The effect of sodium acetate on the interfacial tension of the water–benzene system may be satisfactorily explained by the theory advanced in the previous paper (4) for sodium acetate concentrations less than approximately 2.5 molal. However, the secondary interfacial tension lowering at higher sodium acetate concentrations is a phenomenon which was not encountered in the previous work, probably because the measurements with sodium acetate in the water–toluene systems were not extended to sufficiently high concentrations.

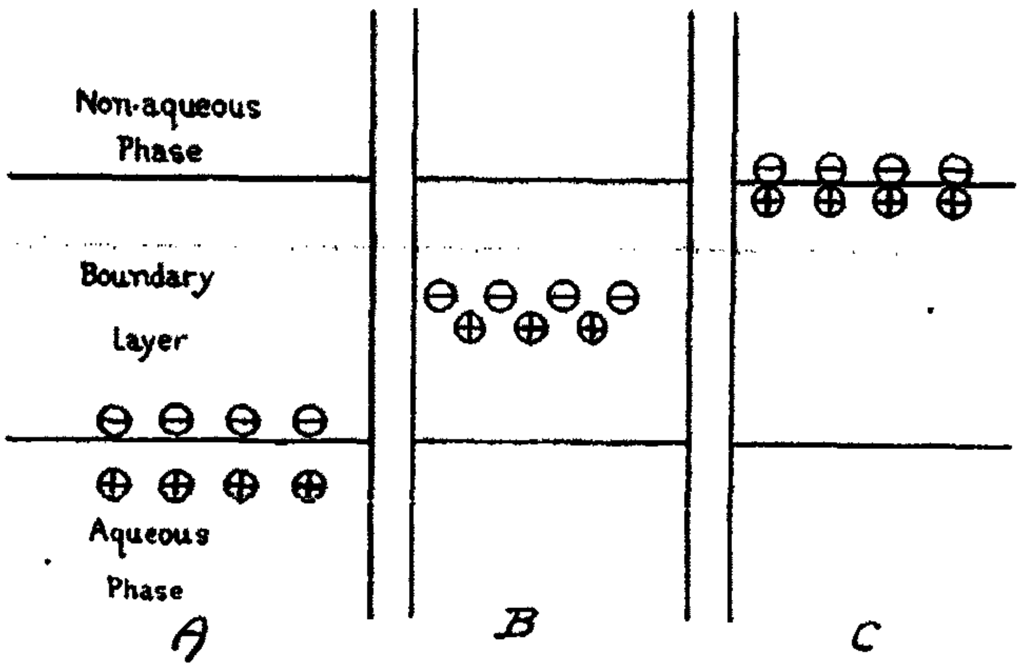

Fig. 4. Diagram of Mean Positions of Effective Ions in Boundary Layer

This secondary lowering effect is probably due to the fact that the ions in the boundary layer approach or enter the oil phase as the concentration of salt in the aqueous phase is increased. In this region, the ions tend to form doublets, owing to their greater electrostatic attraction for each other in the medium of much lower dielectric constant. When the tendency to form doublets becomes sufficiently pronounced, the salt in the boundary layer behaves essentially as a surface active non-electrolyte, lowering the interfacial tension. While other ions are present in the water-like portion of the boundary layer, it is probable that their distribution is sufficiently random to prevent any considerable increase in boundary tension due to their presence.

The theory advanced in this and the previous paper (4) to explain the effect of strong electrolytes on the boundary tension of two phase systems is indicated in a purely diagrammatic way in figure 4. In this figure *A* indicates the postulated mean positions of the effective ions which result in the initial boundary tension lowering, *B* indicates their mean positions for elevation of the boundary tension, and *C* represents their mean positions when the secondary lowering is produced at high concentrations.

It is to be expected that the salt concentration at which the minimum and maximum in the interfacial tension–concentration curve occur, and, therefore, the concentration at which the secondary lowering begins, decreases as the tendency of the negative ion to pass into the non-aqueous phase increases. This statement is borne out by the results given in the previous paper (4) on the water–toluene system. Thus in dealing with the sodium salts of the fatty acids, the positions of the minimum and of the maximum points on the curves would shift to lower salt concentrations as the molecular weight of the fatty acid ion is increased. This is probably the reason that a similar type of effect has not been discovered for the soaps on the boundary tension of water–vapor and water–oil systems. The minima and maxima probably occur at such low concentrations that only the secondary lowering effect has been observed. The fact that the negative ions of the soap polymerize to form colloidal particles should not affect the mechanism of the boundary effect. The greater tendency of acetate ions to pass into mineral oil rather than into toluene or benzene may explain the failure to observe a minimum and a maximum in the sodium acetate curve for the water–mineral oil systems in the preceding work (4).

In general the concentration at which the minimum and maximum occur in any given system would be expected to increase with rising temperature, owing to the increased thermal agitation of the ions in the boundary layer.

It seems probable that this proposed mechanism will be sufficient to explain the effect of all strong electrolytes on the boundary tension of their aqueous solutions. Thus, any solute which is a strong electrolyte when dissolved in water will cause the initial lowering of interfacial tension and the subsequent increase at higher concentrations, provided one ion has a greater tendency than the other to leave the aqueous phase and go into the non-aqueous phase. This is strikingly illustrated by the results of measurements by Traxler and Pittman (5) of the effect of dissolved sodium chloride on the boundary tension of water–asphalt systems. Failure to observe this effect for many other electrolytes is probably due to the fact that careful measurements have not been extended to sufficiently low concentrations.

After the initial decrease and subsequent increase in boundary tension, the effect of strong electrolytes at still higher concentrations depends on an additional factor. This factor is the tendency of the electrolyte as a whole to pass through the boundary layer into the non-aqueous phase as doublets or undissociated molecules. If this tendency is appreciable, the secondary lowering effect will be obtained. Otherwise, the boundary tension will continue to rise with increasing electrolyte concentration in the aqueous phase. Thus, salts of most organic acids probably give the secondary lowering effect at the water-organic liquid boundary on account of their tendency to pass into the organic liquid as undissociated molecules. Salts of organic acids which are very soluble in water probably do not give the secondary lowering effect at the water-vapor boundary. However the soaps do give this effect, owing to their tendency to form a third phase on the vapor side of the boundary layer.

Of the inorganic electrolytes, hydrogen chloride, hydrogen bromide, hydrogen nitrate, hydrogen sulfate, and other electrolytes which tend to pass into the vapor phase as undissociated molecules, exhibit the secondary tension lowering effect at the water-vapor boundary at high concentrations. Non-volatile electrolytes, including practically all salts, increase the surface tension of water at high concentrations. The increase, as has been mentioned previously, depends on the difference between the tendencies of the two ions to leave the aqueous phase as ions.

Other phases of the problem of boundary phenomena are being investigated as rapidly as is possible both in this laboratory and at the State University of Iowa.

SUMMARY

1. Accurate measurements have been made of the effect of dissolved sodium acetate on the interfacial tension of the water-benzene system.

2. The curve obtained by plotting the interfacial tension of this system against the concentration of sodium acetate shows, at high concentrations, a secondary tension lowering effect which has not been observed in previous work.

3. The theory of Eversole and Dedrick has been extended to include the boundary effects of strong electrolytes at higher concentrations.

4. The effects noted in this work appear quite analogous to those described by Taylor (6) in his theory of activated adsorption of gases by solids.

The authors wish to express their sincere appreciation for the very valuable suggestions and criticisms given by Dr. W. G. Eversole of the State University of Iowa.

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NEW BOOKS

L'Architecture de l'Univers. By P. Couderc. Paris: Encyclopedie Gauthier Villars, 1930.

As the title indicates, the present volume, No. 6 in the series, attempts to describe the structure of the visible universe, but a glance at the table of contents indicates that the development of the universe also is included—in its widest cosmogonical aspects. It is not meant as a text book, and indeed it more resembles a collection of selected chapters, the first of which, without much preliminary, really disposes of the question of the structure of our Milky Way system.

A second chapter is devoted to a description of methods, terminology, and some related chemical and physical facts and laws. Chapter III treats of the spectral classification in detail and more specifically of the now defunct theory of stellar evolution, while chapter IV continues this with the Laplace-Jeans theory of the evolution of spiral nebulae, and Jeans's tidal theory for the origin of the planets. With a rather prolonged excursion into the geological evidence for the age of the earth, the probable ages of the stars and the time scale of the universe derived from double stars and clusters are discussed. This naturally leads to relativity, and its bearing upon astronomical space and cosmogony. The last two chapters deal with cosmic rays and the problem of life outside the earth.

The work is illustrated by eight excellent full-page photographs of star fields, clusters, and spiral nebulae. The principal criticism that might be advanced against it is that nearly all theories are presented as if they were final, without much comment or critical analysis. Thus, on p. 144 it is stated quite calmly that epidemics of "grippe" on the earth may well have a *cosmic* origin. An unfortunate slip on p. 103 states that the *inclination* of the earth's axis on the ecliptic varies in 26,000 years, and this may explain the periodic return of glacial epochs.

W. J. Luyten.

Annual International Tables of Constants and Numerical Data, Chemical, Physical, Biological, and Technological. Paris: Gauthier Villars et Cie. New York: McGraw-Hill Book Co., Inc.

Volume VIII, Literature of 1927–28 (published 1931-32) 4-to Part I. xl + 1101 pp. Part II. xxi + 1102–2706 pp. Cloth.

Volume IX, Literature of 1929 (published 1931) 4-to i + 1607 pp. Cloth.

Numerical Data of Spectroscopic Literature of 1925–26. (Extract from Vol. VII of Annual International Tables) (published 1930). 4-to xix, 414–927 pp. Boards.

Index to volumes of the 1st series (I to V, 1910–1922) (published 1930). Compiled by G. Kravtzoff. 4-to lxii + 382 pp. Cloth.

Index to Volume IX. Literature of 1929 (published 1932). Compiled by G. Kravtzoff. 4-to xxiv + 124 pp. Boards.

These volumes represent a continuation of the activities of an International Committee appointed by the 7th Congress of Applied Chemistry (London, 1909) and continued under the auspices of the International Research Council and the International Union of Chemistry. Dr. Ch. Marie, Secretary General of the International Committee, has unstintingly devoted his energies to the task of making this project a success, and he merits the sincere thanks of all workers in the field of the chemical and physical sciences.

The scope of the work as represented in the earlier publications is so well known to scientists that an extended review of the present volumes is unnecessary. In these days when scientific data are scattered through a thousand "journals" it becomes imperative that someone undertake the task of collecting those data which appear to possess more or less permanent value and making them available to the researcher in some such form as those publications represent.

It is a necessary consequence of this type of publication that volumes such as these should be rather expensive. However, their cost would represent an insignificant fraction of the cost of the time which the industrial or research worker without them would spend in searching the literature, so that the initial cost for their purchase will eventually be returned manyfold. It is an interesting commentary on human nature that the governing body of an organization will often quibble over a very moderate expenditure for books and at the same time spend without a question thousands of dollars for machinery, equipment, or new personnel. The library is the heart of a university or of a research laboratory, and volumes such as these are an invaluable adjunct to abstract journals.

Special attention should be called to the index volumes, the first being a collective index for Vols. I to V. More than twenty thousand substances are classified here. It contains (1) an analytical index alphabetically arranged in four languages (in parallel columns), (2) an alphabetical index of all substances (animal, plant, mineral, technologic products, etc.) including many chemical "trade names" which the chemist does not always associate with the chemical formula, and (3) a formula index, (arranged according to empirical formulas) of all definite chemical compounds.

These volumes, and those which preceded and those which will follow, should be on the shelves of every reference library and of the library of every research institution. Special prices may be secured by taking advantage of the subscription rates. Incidentally, it may be noted that certain sections (note, *e.g.*, section on spectroscopic data noted above) may be purchased separately if purchase of the entire volume is not desired.

Ross Aiken Gortner.

Einführung in die Elektronik. By O. Klemperer. 25.5 × 17 cm.; xii + 304 pp. Berlin: Springer, 1933. Price: unbound, 18.60 marks; bound, 19.80 marks.

The sub-title is "The experimental physics of the free electron in the light of classical theory and of wave mechanics." The experimental side of the subject is stressed throughout, the mathematical and theoretical sides being merely quoted in sufficient detail to give point to the story. Problems involving relatively abstruse sections of electron-gas kinetic theory are handled either very briefly, or not at all; there is, for example, no mention of thermoelectricity.

So far as concerns the mere experimental side of our acquaintance with the properties of the negative electron, the book may not inaptly be described as a small "Encyclopaedia Electronica." It deals with a wide range of very diverse phenomena, here grouped for convenience—and of necessity somewhat arbitrarily—under three main headings: (1) the free electron; (2) electron emission; and (3) interaction between free electrons and atoms. The treatment, in a single volume of this size, is naturally not exhaustive (in the account of Millikan's oil-drop experiments, for instance, the question of the validity of Stokes' law is dismissed in a brief footnote), but the text is supplemented by well-chosen references to original papers.

The value of the work is enhanced, for many classes of readers, by the inclusion of a good selection of numerical tables, ranging from atomic structure factors to data on sensitivities of photographic emulsions to electrons of different speeds. The numerical data quoted are generally based on the most recent determinations of the relevant fundamental constants—though, as a minor criticism, it appears somewhat inconsistent to quote the round figure of 300 volts as the equivalent of 1 E.S.U. of potential difference, while stressing the distinction between absolute and international electrical units.

Taken as a whole, the book may be recommended as an excellent introduction to —and, for non-specialists, an adequate summary of—the greater part of experimental electronics. There was a real need for a compilation of this character, and Dr. Klemperer's book fills a very definite gap in the literature of his subject.

H. R. ROBINSON.

Actualités Scientifiques et Industrielles, 51 et 52. By M. G. URBAIN. Théories chimiques, publiées sous la direction de M. G. Urbain. I et II. La coördination des atomes dans la molecule; la symbolique chimique. 51 and 52 pp. Paris: Hermann et Cie, 1933. Price: 12 francs each.

In this beautifully and clearly written monograph, Professor Urbain, using a historical background, attempts to bring the theories of inorganic and organic chemists about the structure of chemical compounds to a common basis. In general, he thinks that the theories of structure in inorganic chemistry have rested on a molecular *pluraliste* basis, beginning with the electrochemical theory of Berzelius, and, after that was abandoned following the discovery of substitution by Dumas, revived in a modified form many years later in the coördination theory of Werner.

He thinks of the structures of organic chemists as referring everything to attractions between atoms without any thought of electrical forces, beginning with the substitutions of Dumas, through the types of Gerhardt—Laurent is not mentioned—and the atomic linkings of Kekulé. Frankland and Couper are omitted but a complete picture is not to be expected in so brief a monograph.

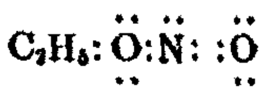
Professor Urbain sums up his conclusions in three sentences, (p. 40, Part II): (1) Neutral molecules may be formed with electrovalent unions. (2) Neutral molecules may be formed with non-electrovalent unions. (3) When a molecule contains both electrovalent and non-electrovalent unions, such a molecule should be considered as a complex molecule in which the constituent parts belong to the first two classes.

Among the "electrovalent" unions Professor Urbain includes the union between hydrogen and carbon in methane and many other unions which American and English chemists consider as covalent. He thinks of the electron as transferred from the hydrogen to the carbon and that there is hidden *dissimule* ionization in such cases (Part I, p. 26; Part II, pp. 19 and 21). In this he follows, without knowing it, the interpretation of Kossel's electronic theory, which has been made the basis of articles in the Chemisch Weekblad by van Arkel and de Boer, published in a German translation. Such a point of view confuses covalences with genuine ionic valences, though the latter may be found in compounds in "semi-ionic" unions and in complex molecules.

Closely connected with this confusion is his failure to see (Part I, p. 32 and elsewhere), that Meisenheimer has demonstrated that the fourth and fifth valences of quinquevalent nitrogen are different. The fourth is a covalence similar to the three covalences of ammonia, while the fifth is a positive ionic valence.

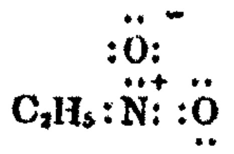
In a similar manner (Part I, p. 49), while he sees clearly that if the chlorine of triethylsulfonium chloride is united by a covalence to the sulfur atom that atom would have ten instead of eight electrons in its outer shell, he has not understood that when a sulfur atom takes on a third covalence it becomes a positive ion, just as the nitrogen of ammonia becomes a positive ion when it takes on a fourth covalence.

It was hardly to be expected that Professor Urbain should know that alkyl nitrites and the isomeric nitro compounds have quite different electronic structures. Ethyl nitrite is



$$\mathrm{C_2H_5}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\ddot{\mathrm{N}}:\,:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}$$

and boils at 17°C. Nitroethane is



$$\begin{array}{c}\quad:\ddot{\mathrm{O}}:^{-}\\ \mathrm{C_2H_5}:\overset{+}{\ddot{\mathrm{N}}}:\,:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}\end{array}$$

and boils at 114°C. This makes his reasoning about the structure of these compounds fallacious (Part II, p. 26). Silver nitrite gives, with alkyl halides, alkyl nitro compounds by an electronic and molecular rearrangement.

The author of the monograph seems (Part II, pp. 36–39) to confine the term "non-electrovalent" to bonds between atoms of the same kind. He is unable to furnish any definite electrical or electronic interpretation of such bonds. van Arkel and de Boer, in the book referred to, acknowledge the same difficulty. The theory of shared electrons proposed by G. N. Lewis in 1916 gives a very satisfactory explanation for this difficulty, and that theory has been given a kinetic interpretation by Noyes, Campbell, Sidgwick, C. A. Knorr, and others, and a quantum mechanics interpretation by Slater, Linus Pauling, and others. That theory enables us to foresee, instead of a single neutral methyl discussed by Urbain, three kinds of methyl for which there is good experimental evidence: positive methyl formed by the ionization of methyl iodide when the methyl adds to the sulfur atom in the formation of trimethylsulfonium iodide; neutral methyl with an odd electron formed by the electrolysis of sodium acetate and by dissociations; and negative methyl, formed by the ionization of one of the bonds of ethylene to permit the positive chlorine of hypochlorous acid to unite with it while the negative hydroxyl unites with the positive methyl.

The most serious criticism of the book is the failure to make any reference to the theory of coördination proposed by Sidgwick, who ascribes it to covalences in his book on "The Electronic Theory of Valency." Professor Urbain comes surprisingly close to this when he compares the stereochemistry of the optically active compounds of carbon with that of the optically active complexes. His ideas of non-electrovalent structures prevent him from reaching a satisfactory conclusion. Sidgwick has presented an electronic theory based on that of Lewis and Langmuir which makes it applicable to all the chemical elements and all compounds. A somewhat modified exposition of that theory of inorganic complexes will be presented soon in The Journal of the American Chemical Society by the author of this review.

W. A. Noyes.

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